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THE ENTHALPY OF FORMATION OF ARSINE

S. M. Ariya, M. P. Morozova and Khuan Tszi-tai

The enthalpy of formation of arsine has more than once been the subject of investigation by a series of authors [1, 2]. At the present time the universally adopted figure [3-5] found by Ogier [2] is 43.6 kcal/mole.

The author cited [2] used for the calorimetric measurements the reaction of arsine with liquid bromine and water. Berthelot and Petit [6], by the same method, found the enthalpy of formation of stibine to be 79.5 kcal/mole. Stock and Wrede [7], by spontaneous decomposition of stibine (initiated ignition from a high voltage coil) in a calorimeter, found a much lower absolute value, namely 34 kcal/mole. Stock and Wrede showed that the method indicated by Ogier was incorrect and therefore the figure proposed by him for the enthalpy of formation of arsine is not true.

In the determination of the enthalpy of formation of AsH_3 by spontaneously carrying out its decomposition reaction in a calorimeter, the high stability of this substance, which decomposes very slowly even at temperatures of 500° or thereabouts, with an electrical discharge, is a hindrance.

We obtained the value for the enthalpy of formation of arsine by calorimetric determination of the enthalpy of the reaction between magnesium arsenide and dilute hydrochloric acid, the reaction between magnesium arsenide and dilute hydrochloric acid containing potassium iodide and iodine, and the enthalpy of mixing of a solution of arsenic acid with dilute hydrochloric acid containing potassium iodide and iodine.

The first reaction proceeds according to the equation:

$$Mg_3As_{2\,\mathrm{cryst.}} + 6HCl_{\mathrm{sol.}} = 3MgCl_{2\,\mathrm{sol.}} + 2AsH_{3\,\mathrm{gas}}$$

The second reaction proceeds without evolution of gas; the state of valency of the arsenic present in the products is not clear. In order to avoid errors connected with this uncertainty, we determined the heat of mixing of a solution of arsenic acid with the same solution ($HCl + KI + I_2$) in which the dissolution of Mg_3As_2 had been produced.

This offers the possibility of determining the heat of formation of arsine with the aid of the following series of reactions:

$$Mg_3As_{2\,\mathrm{cryst.}} + 6HCl_{\mathrm{sol.}} = 3MgCl_{2\,\mathrm{sol.}} + 2AsH_{3\,\mathrm{gas}} + Q_1.$$

$$2AsH_{3\,\mathrm{gas}} = 2As_{\mathrm{cryst.}} + 3H_{2\,\mathrm{gas}} + Q_2$$

$$2As_{\mathrm{cryst.}} + 8H_2O_{\mathrm{liq.}} + 5(KI + I_2)_{\mathrm{sol.}} = 5KI_{\mathrm{sol.}} + 2H_3AsO_{4\,\mathrm{sol.}} + 10HI_{\mathrm{sol.}} + Q_3,$$

$$3H_{2\,\mathrm{gas}} + 3(KI + I_2)_{\mathrm{sol.}} = 6HI_{\mathrm{sol.}} + 3KI_{\mathrm{sol.}} + Q_4,$$

$$H_3AsO_{4\,\mathrm{sol.}} + x(KI + I_2)_{\mathrm{sol.}} + yHCl_{\mathrm{sol.}} + zH_2O_{\mathrm{liq.}} = \ldots + Q_5.$$

The sum $Q_1 \ldots Q_5$ represents the magnitude of the heat effect of the reaction of magnesium arsenide with dilute hydrochloric acid containing KI and I_2 (Q).

The amounts Q, Q_1 and Q_5 were determined experimentally by us: Q = 371.1 kcal, Q_1 = 213.6 kcal, Q_5 = 15.2 kcal.

The quantities Q_3 and Q_4 may be easily calculated on the basis of the data given in the literature [3]: Q_3 = 25.7 kcal, Q_4 = 85.6 kcal.

The quantity required $Q_2 = 371.1 - 213.6 - 25.7 - 85.6 - 15.2 = 31.0$ kcal.

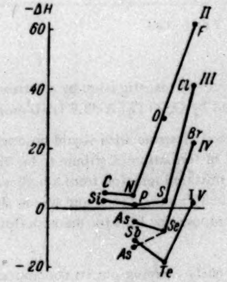

Fig. 1. Enthalpy of formation of volatile hydrogen compounds (referred to 1 g-atom of hydrogen) for elements of groups II – IV of the periodic system (in kcal).

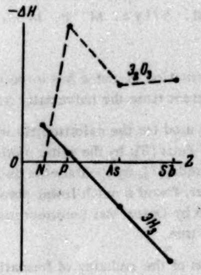

Fig. 2. Enthalpy of formation of hydrogen and oxygen compounds of elements of main sub-group of group V (in kcal/mole) as a function of the ordinal number (Z).

From this the enthalpy of formation of arsine is shown to be (at 298°K), 15.5 ± 4 kcal/mol.*

$$As_{cryst.} + \frac{3}{2} H_{2\,gas} = AsH_{3\,gas} - 15.5 \text{ Kcal.}$$

The slightly higher error connected with this amount is explained by the large amounts involved in its calculation.

Fig. 1 represents the enthalpy of formation of volatile hydrogen compounds referred to 1 g-atom of hydrogen, for the first five groups of the periodic system. The points shown on a line are based on the preceding value of the enthalpy of formation of arsine(43.6 kcal).

When using the new value for arsine, the usual course of the measurements, (referred to 1 g-atom of hydrogen) of the enthalpy of formation of hydrogen compounds, in passing from an element of the sixth group to an element of the fifth group, is observed. Previous knowledge of the enthalpy of formation of arsine created an impression of anomalous behavior for elements of group IV.

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*Later, by determining the heat of the reaction:

$$Zn_3As_{2\,cryst.} + 6HCl_{sol.} = 3ZnCl_{2\,sol.} + 2AsH_{3\,gas}$$

$$Zn_3As_{2\,cryst.} + aHCl_{sol.} + bBr_{2\,liq.} = 3ZnBr_{2\,sol.}$$

$$As_{cryst.} + cHCl_{sol.} + dBr_{2\,liq.} = \ldots$$

we found 18 ± 1.5 kcal/mole for ΔH of formation of AsH_3. As this method involves smaller quantities, we prefer 18 ± 1.5 kcal/mole for the ΔH of formation of arsine.

Fig. 2 represents the course of the amounts for the enthalpy of formation of hydrogen compounds of elements of the main subgroup of group V, as a function of the ordinal number. This curve is practically linear, i. e., the phenomenon of secondary periodicity is not extended at all to the enthalpy of formation of hydrogen compounds of elements of the main subgroup of group V, or only very weakly. For comparison, in Fig. 2 is given the curve for the enthalpy of formation of oxygen compounds of elements of the main sub group V and this clearly obeys the rule of secondary periodicity.

SUMMARY

1. The enthalpy of formation of arsine has been found to be 18 ± 1.5 kcal/mole (at 298°K).

2. The enthalpies of formation of hydrogen compounds of elements of the main subgroup of group V represent approximately a linear function of the ordinal number. The effect of secondary periodicity is thus not extended at all to the hydrogen compounds of elements of the main subgroup of group V or only very slightly.

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[4] E. V. Britske and A. F. Kapustinsky (Ed), Thermal Constants of Inorganic Substances (Moscow, 1949).

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Leningrad State University.

Fig. 8 represents the course of the [illegible] for the enthalpy of formation of hydrogen compounds of elements of the main subgroup of group V as a function of the atomic number. This curve is practically linear, i.e., the phenomenon of secondary periodicity is not expressed at all in the enthalpy of formation of hydrogen compounds of elements of the main subgroup of group V [illegible]. For comparison, in Fig. 8 is given the curve for the enthalpy of formation of oxygen compounds of elements of the [illegible] which closely obeys the rule of secondary periodicity.

SUMMARY

1. The enthalpy of formation of [illegible].

2. The enthalpies of formation of hydrogen compounds of elements of the main subgroup of group V represent approximately a linear function of the atomic number. The effect of secondary periodicity is hardly expressed at all in the hydrogen compounds of elements of the main subgroup of group V [illegible].

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[3] Bichowsky and Rossini. Thermochemistry of Chemical Substances (1936).

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Received July 17th, 1954. [illegible]

STUDY OF THE INTERACTION OF SULFATES AND MOLYBDATES OF LITHIUM AND SILVER IN MELTS

I. N. Belyaev and S. S. Doroshenko

Earlier, [1-4] in examples of the sulfate – molybdate and sulfate – tungstate exchange of lead and alkali metals, it was shown that the irreversibility increases in the series of the reciprocal systems Li(Na, K)Pb ‖ SO_4, $WO_4(MoO_4)$ from K, Pb ‖ SO_4, $WO_4(MoO_4)$ to Li, Pb ‖ SO_4, $WO_4(MoO_4)$.

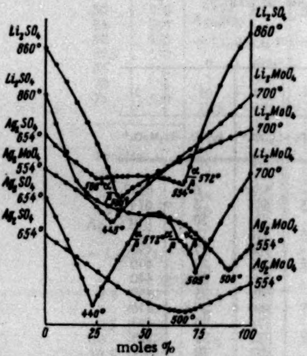

Fig. 1. Fusibility of lateral sides and diagonal sections.

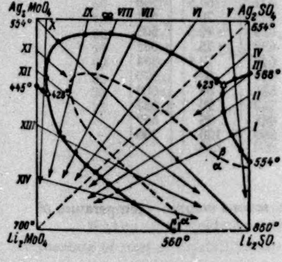

Fig. 2. Course of internal sections.

In these works it was shown that when one of the cations taking part in the reaction has 18 + 2 surface electrons (Pb) and one of the two complex oxygen-containing anions has in its composition an element with an incomplete d - electron film (W, Mo), then the reaction is directed towards the side of combination of the cation with (18 + 2) electron films, with the anion containing the incomplete d-electron film.

The systems investigated, Na, Ag ‖ MoO_4, SO_4 [5] showed that the relationships found for the systems with sharing of the cation with (18 + 2) electron film, extend to systems with an 18-electron film.

In the present paper the results are presented of a study of interaction in the system, sulfates and molybdates of lithium and silver by the visual polythermal method. The fused salts were prepared in a platinum crucible in a resistance furnace, the temperature being regulated with the aid of a Pt – PtRh thermocouple calibrated to the melting point of the chemically pure salt. The melts were stirred vigorously with a platinum stirrer.

There were investigated the salts: Li_2SO_4, chemically pure, m. p. 860°; Li_2MoO_4 obtained by fusing c. p. Li_2CO_3 and MoO_3 in stochiometric proportions; MoO_3 was prepared from ammonium molybdate by heating it to 300-400° and subsequent calcination in an atmosphere of oxygen, m. p. Li_2MoO_4 – 700°, Ag_2SO_4 was obtained according to [6], m. p. 654°; Ag_2MoO_4 was obtained by fusing $AgNO_3$ with MoO_3 according to [7], m. p. 554°. All the salts were dried carefully and stored in an desiccator over sulfuric acid.

Lateral sides. 1. The system $Ag_2SO_4 - Li_2SO_4$ was studied earlier[8, 9]. Our data are given in Fig. 1 and agree with the literature. In the system, one compound is formed in the proportion 1 : 1 and forms eutectic mixtures with the original components of composition 25 mole% and 67mole % Li_2SO_4 *, whose melting points are 568 and 554°. Conversion from α- to β-Li_2SO_4 takes place at 572° and 68.5% Li_2SO_4.

2. The system $Ag_2MoO_4 - Li_2MoO_4$ represents a system with a simple eutectic of composition 32% Li_2MoO_4 and m. p. 445° (Fig. 1. Table 1).

3. The system $Ag_2MoO_4 - Ag_2SO_4$ has been studied earlier [5]. It was considered to be beyond the eutectic although a carefully repeated study showed that the system passes through an uninterrupted series of solid solutions with a minimum at 500° (Fig. 1, Table 1).

4. The system $Li_2MoO_4 - Li_2SO_4$ was studied first of all and is characterized by a simple eutectic of composition 64.5% Li_2SO_4 and m. p. 560°. Conversion from α- to β-Li_2SO_4 takes place at 572° and 67% Li_2SO_4 (Table 1, Fig. 1).

Diagonal sections. The stable diagonal $Ag_2MoO_4 - Li_2SO_4$ has the form of the usual binary system with a eutectic, composition 11% Li_2SO_4 and m. p. 506°. Polymorphic conversion is observed at 572° and 25.5% Li_2SO_4. (Table 1, Fig. 1). As seen from Fig. 1, on the lateral branch of the Li_2SO_4 crystallization, there is a marked sloping portion, indicating the approach of components of the stable pair to the limit of saturation. The unstable section is $Ag_2SO_4 - Li_2MoO_4$ (Fig. 1, Table 1); liquidus curve of the system has four transitional points, corresponding to the joint crystallization: Ag_2SO_4 and β-Li_2SO_4 (440° and 22% Li_2MoO_4); β-$Li_2SO_4 - Li_2MoO_4$ (505° and 72.5% Li_2MoO_4); and two points of common crystallization of α- and β-Li_2SO_4 at 572°.

TABLE 1

Ag_2MoO_4—Li_2MoO_4*		Ag_2MoO_4—Ag_2SO_4*		Li_2MoO_4—Li_2SO_4*		Ag_2MoO_4—Li_2SO_4*		Ag_2SO_4—Li_2MoO_4*	
1	2	1	2	1	2	1	2	1	2
0	554°	0.0	555°	0	700°	0	554°	0	654°
5	540	5	546	5	690	2.5	545	5	614
10	527	10	537	10	682	5	534	10	570
15	512	15	528	15	674	7.5	520	15	521
20	496	20	519	20	664	10	508	17.5	493
25	480	25	510	25	655	12.5	513	20	470
27.5	467	27.5	506	30	646	15	525	22.5	440
30	456	30	503	35	636	20	549	25	459
32.5	448	32.5	500	40	625	22.5	560	27.5	476
35	460	35	501	45	614	25	570	30	493
37.5	473	37.5	502	50	602	27.5	582	35	528
40	485	40	505	55	588	30	592	40	561
45	504	45	510	57.5	582	32.5	599	45	600
50	524	50	518	60	574	35	604	50	620
55	540	55	528	62.5	566	40	612	55	621
60	558	60	538	65	568	45	617	60	606
65	576	65	552	67.5	597	50	620	65	569
70	592	70	565	70	623	55	621	67.5	558
75	609	75	580	72.5	646	60	623	70	541
80	628	80	595	75	669	65	629	72.5	505
85	644	85	610	80	712	70	638	75	535
90	662	90	624	85	753	75	649	77.5	554
95	679	95	639	90	792	80	662	80	570
100	700	100	654	95	826	85	686	85	603
				100	860	90	742	90	637
						95	801	95	669
						100	860	100	700

Note: First column — mole % of added component (indicated by an asterisk), second column — temperature of start of crystallization.

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* All percentages are molecular.

TABLE 2

Section I

$$\left.\begin{array}{c}50\%\\ \mathrm{Li_2SO_4}\\ 50\%\\ \mathrm{Ag_2SO_4}\end{array}\right\}\rightarrow$$

→ Li_2MoO_4 *

1	2
0	574°
2.5	539
5	511
7.5	485
10	496
12.5	518
15	536
20	567
25	608
30	625
35	633
40	629
45	614
50	586
55	558
60	526
62.5	530
65	542
70	564
75	587

Section II

$$\left.\begin{array}{c}35\%\\ \mathrm{Li_2SO_4}\\ 65\%\\ \mathrm{Ag_2SO_4}\end{array}\right\}\rightarrow$$

→ Li_2MoO_4 *

1	2
0	572°
2.5	547
5	521
7.5	498
10	469
12.5	455
15	476
20	516
25	556
30	596
35	619
40	625
45	622
50	609
55	581
60	554
65	526
70	539
75	572

Section III

$$\left.\begin{array}{c}25\%\\ \mathrm{Li_2SO_4}\\ 75\%\\ \mathrm{Ag_2SO_4}\end{array}\right\}$$

→ Li_2MoO_4 *

1	2
0	568°
2.5	534
5	507
7.5	481
10	460
12.5	440
15	456
17.5	470
20	484

Section IV

$$\left.\begin{array}{c}15\%\\ \mathrm{Li_2SO_4}\\ 85\%\\ \mathrm{Ag_2SO_4}\end{array}\right\}\rightarrow$$

→ Li_2MoO_4 *

1	2
0	600°
5	542
10	482
12.5	459
15	436
17.5	449
20	465
25	500
30	533
35	562
40	604
45	621
50	623
55	611
60	579
65	554
67.5	537
70	509
72.5	530
75	548

Section V

$$\left.\begin{array}{c}90\%\\ \mathrm{Ag_2SO_4}\\ 10\%\\ \mathrm{Ag_2MoO_4}\end{array}\right\}$$

→ Li_2SO_4 *

1	2
0	624°
5	599
10	571
15	546
20	520
22.5	506
25	489
27.5	472
30	483
32.5	492
35	500
40	511
45	515
50	516
55	514
60	512
62.5	510
65	545
67.5	562
70	583
75	648
80	696

Section VI

$$\left.\begin{array}{c}25\%\\ \mathrm{Ag_2MoO_4}\\ 75\%\\ \mathrm{Ag_2SO_4}\end{array}\right\}\rightarrow$$

→ Li_2MoO_4 *

1	2
0	580°
5	538
10	497
12.5	479
15	460
17.5	465
20	483
25	518
30	548
35	570
40	604
45	620
50	622
55	600
60	568
65	542
67.5	517
70	521
72.5	540
75	556

Section VII

$$\left.\begin{array}{c}50\%\\ \mathrm{Ag_2MoO_4}\\ 50\%\\ \mathrm{Ag_2SO_4}\end{array}\right\}$$

→ Li_2MoO_4 *

1	2
0	518°
2.5	500
5	486
7.5	474
10	480
12.5	498
15	515
20	542
25	560
30	581
35	607
40	613
45	606
50	582
55	561
60	532
62.5	506
65	516
70	550
75	574

Section VIII

$$\left.\begin{array}{c}37.5\%\\ \mathrm{Ag_2SO_4}\\ 62.5\%\\ \mathrm{Ag_2MoO_4}\end{array}\right\}$$

→ Li_2MoO_4 *

1	2
0	502°
2.5	492
5	484
7.5	482
10	500
12.5	513
15	526

Section IX

$$\left.\begin{array}{c}25\%\\ \mathrm{Ag_2SO_4}\\ 75\%\\ \mathrm{Ag_2MoO_4}\end{array}\right\}\rightarrow$$

→ Li_2MoO_4 *

1	2
0	510°
2.5	506
5	499
7.5	494
10	506
15	527
20	547
25	566
27.5	576
30	585
35	578
40	559
45	536
50	508
52.5	493
55	487
57.5	505
60	523
65	550
70	571
75	592

Section X

$$\left.\begin{array}{c}5\%\\ \mathrm{Ag_2SO_4}\\ 95\%\\ \mathrm{Ag_2MoO_4}\end{array}\right\}\rightarrow$$

→ Li_2MoO_4 *

1	2
0	546°
5	536
10	523
15	508
20	495
30	463
25	481
32.5	450
35	441
37.5	454
40	467
45	491
50	512
55	532
60	552
65	563

Section XI

$$\left.\begin{array}{c}15\%\\ \mathrm{Li_2MoO_4}\\ 85\%\\ \mathrm{Ag_2MoO_4}\end{array}\right\}$$

→ Li_2SO_4 *

1	2
0	512°
2.5	504
5	498
7.5	515
10	532
15	559

Section XII

$$\left.\begin{array}{c}25\%\\ \mathrm{Li_2MoO_4}\\ 75\%\\ \mathrm{Ag_2MoO_4}\end{array}\right\}$$

→ Li_2SO_4 *

1	2
0	480°
2.5	477
5	474
7.5	505
10	526
15	560
20	584
25	597
30	607
35	614
40	616
45	617
50	618
55	620
60	623
65	628
70	639
75	654

Section XIII

$$\left.\begin{array}{c}50\%\\ \mathrm{Li_2MoO_4}\\ 50\%\\ \mathrm{Ag_2MoO_4}\end{array}\right\}\rightarrow$$

→ Li_2SO_4 *

1	2
0	524°
5	507
10	492
15	500
20	530
25	547
30	558
35	566
40	570
45	574
50	583
55	592
60	602
65	614
70	627
75	644

Section XIV

$$\left.\begin{array}{c}75\%\\ \mathrm{Li_2MoO_4}\\ 25\%\\ \mathrm{Ag_2MoO_4}\end{array}\right\}$$

→ Li_2SO_4 *

1	2
0	608°
5	598
10	590
15	588
20	574
25	566
30	557
35	548
40	536
45	524
50	538
55	554
60	564
65	571
70	608
75	650

Note: First column – mol. % of added component (indicated by an asterisk), second column – temperature of start of crystallization.

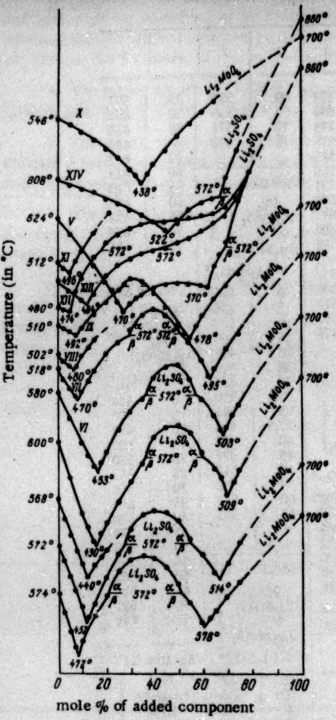

Fig. 3. Fusibility of internal sections. Explanation in Tables 2, 3.

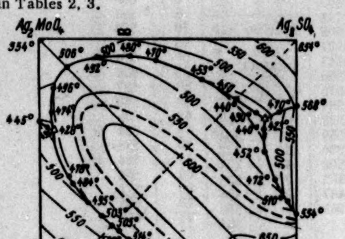

Fig. 4. Projection of three-dimensional diagram on composition square.

For the explanation of the primary phase of crystallization in the system, apart from the lateral sides and the diagonal sections, 14 internal sections were studied, the course of which is shown in Fig. 2. The fusibility data of the sections are given in Fig. 3 and Table 2.

From the fusibility data for the lateral sides and the diagonal internal sections, a projection was constructed of the surface of crystallization by a three-dimensional diagram on the composition square (Fig. 4). For determining more accurately the non-variable points and the isotherm of the crystallization surface, projections were constructed of the line of common crystallization on the side of a square (Fig. 5); the upper – on the $Li_2MoO_4 - Li_2SO_4$ side, the lower – the $Li_2SO_4 - Ag_2SO_4$ side.

As seen from Fig. 4, the system is shown to be mutually irreversible, with a stable diagonal section $Li_2SO_4 - Ag_2MoO_4$. One of the salts of the stable part (Ag_2MoO_4) contains a cation with an 18-electron film and an element with an irreversible d-electron film.

A comparison of the diagrams in Fig. 4 with the diagrams of the system Na, Ag ‖ SO_4, MoO_4 [5], shows that the irreversibility in the system Ag, Li ‖ MoO_4, SO_4 is expressed more sharply than in the system Na, Ag ‖ SO_4, MoO_4. In the system Li, Ag ‖ MoO_4, SO_4 on the surface of crystallization, Li_2SO_4 has a fairly large area, being almost a horizontal square, indicating the approach to the saturation limit and the possibility of separation.

In this way, a study of the system once again illustrates the rules formed earlier with reference to the direction of the reaction of sulfate-molybdate exchange in the field of the alkali metals and metals endowed with cations with 18 or (18 + 2) electron films [5].

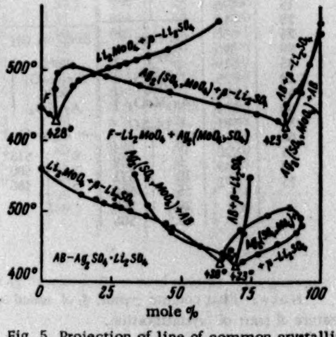

Fig. 5. Projection of line of common crystallization on side of composition square.

The complex compound on the $Ag_2SO_4 - Li_2SO_4$ side, as seen from Fig. 4, does not show any marked effect on the exchange reaction, its role of crystallization occupying a comparatively insignificant part in any surface of crystallization of the system.

SUMMARY

1. The reciprocal-irreversible system of sulfates and molybdates of lithium and silver has been studied by the visual polythermal method. $Ag_2MoO_4 - Li_2SO_4$ appears to be the stable pair.

2. It is shown that in the series of the irreversible systems Li, (Na) Ag ‖ SO_4, MoO the irreversibility increases from Na to Li.

3. There has been confirmed the assumption formulated earlier, that, in the sulfate–molybdate exchange of alkali metals with cations with 18 – and (18 + 2) electron films, the reaction is directed to the side of the union of the cation with 18 – or (18 + 2) internal electron films with anions containing in their composition an element with an irreversible d-electron surface.

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Rostov-on-Don State University.

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The variables considered in the [illegible] effect on the [illegible] reaction [illegible] surface or crystallization of the system.

SUMMARY

1. The technique of [illegible]

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STUDY OF THE MECHANISM OF DISTRIBUTION OF ISOMORPHOUS COMPONENTS ON CRYSTALLIZATION FROM AQUEOUS SOLUTIONS USING RADIOACTIVE INDICATORS

I. STUDY OF THE EQUILIBRIUM IN THE SYSTEM COPPERAMMONIUM SULFATE – ZINCAMMONIUM SULFATE – WATER AT 20° IN PRESENCE OF THE RADIOACTIVE ISOTOPES Zn^{65} AND Cu^{64}

G. I. Gorshtein and N. I. Silantyeva

The problem of the mechanism of distribution of isomorphous components between solid and liquid phases on crystallization from aqueous solutions, is of considerable importance in all the different fields of science and practice. A study of equilibrium in aqueous salt systems with isomorphous components forming true solid solutions has been carried out and at the present time it is proceeding in two different directions. The first of these had its beginning in the work of Vant Hoff and Rosebaum.

It is being concluded by a study of the equilibrium in systems at macroconcentrations of both components in the solid phase and salt fractions of mother liquors (we accept provisionally the limit between the micro- and macroconcentrations of about 1% of each of the isomorphous components with respect to their sum). For this, the authors usually arrange tables and diagrams of the compositions of the solid phases and the mother liquors and diagrams of "distribution" of the isomorphous components between the solid and liquid phases. Only in a few cases have attempts been made to explain the general rules of distribution of isomorphous components.

The second trend developed in 1924 in the classical researches of the school of V. G. Khlopin in a study of the mechanism of equilibrium distribution in aqueous-salt systems for micro-concentrations of one of the isomorphous components (in the capacity of microcomponents, usually salts of natural radioactive elements, mainly radium, were used).

The school of V. G. Khlopin established the linear rule of equilibrium distribution of isomorphous components between solid and liquid phases in concentrations up to approximately 10^{-2} mol.% with reference to the principal substance.

The problem of concentration limits with respect to the application of the linear law of distribution and the mechanisms of distribution in passing from microconcentration to macroconcentration of each of the isomorphous components, remained open.

Systematic experimental investigations [1-3] were first started by us in this direction. It was shown on a series of isomers that the limits of application of the linear law of distribution are considerably wider than has been assumed hitherto. Moreover, it was established that many three-component aqueous-salt systems with isomorphous and isodimorphous components, are ideal for the desired micro- and macroconcentrations of both salt components in the fields of existence of solid phases of definite structure.

The use of synthetic radioactive isotopes as radioactive indicators opens up new perspectives of investigation of both mechanisms of equilibrium distribution of isomorphous components at micro- and macroconcentrations. In the present communication, radiation results are reported of our first experimental work in this direction.

The system $CuSO_4 \cdot (NH_4)_2SO_4 - ZnSO_4 \cdot (NH_4)_2SO_4 - H_2O$ was studied at 25° by Hill and colleagues [4] for macroconcentrations of both isomorphous components. The authors used the methof of "recrystallization" – prolonged mixing of a solution of one of the components with granular crystals of the other component.

We calculated the magnitude of the equilibrium distribution coefficients of zinc salts with reference to copper salts, according to Hill's data $D_{Zn/Cu} = \frac{c_{Zn\ sol.}}{c_{Cu\ sol.}} : \frac{c_{Zn\ liq.}}{c_{Cu\ liq.}}$ and the reverse amounts $D_{Cu/Zn}$, where c_{Zn} and c_{Cu} are the concentrations of the zinc and copper salts in the solid phases (sol.) and in the mother liquors (liq). The results of these calculations are given in Table 1.

TABLE 1

Figures for the Equilibrium Distribution Coefficients in the System $CuSO_4 \cdot (NH_4)_2 - ZnSO_4 \cdot (NH_4)_2SO_4 - H_2O$ According to Hill's Experimental Data

Content in mother liquor (%)		Content in solid phase (%)	$D_{Cu/Zn}$	$D_{Zn/Cu}$
$CuSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	$ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	$CuSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$		
25.26	0.00	100.00		
20.21	3.27	70.90	0.40	2.5
20.32	3.16	68.57	0.35	2.8
16.43	5.65	50.27	0.35	2.9
16.43	5.65	49.98	0.34	2.9
10.71	9.27	22.56	0.25	4.0
10.73	9.24	22.50	0.25	4.0
5.86	12.61	4.84	0.11	9.1
5.89	12.64	3.52	0.08	12.7

In agreement with Hill's experimental data, the system is not an ideal one, since deviations from an ideal substance are considerable: the amount $D_{Zn/Cu}$ varies from 2.5 to 12.8, correspondingly, the reverse quantity $D_{Cu/Zn}$ varies from 0.40 to 0.08. On the basis of the results of our investigations on the distribution of isomorphous components in some systems with binary salts of the schoenite type, [3], doubts arose as to the accuracy of Hill's experimental data and we decided to carry out an experimental check.

Our investigations of the system $CuSO_4 \cdot (NH_4)_2SO_4 - ZnSO_4 \cdot (NH_4)_2SO_4 - H_2O$ were carried out at 20 and 25°.

Determinations of the equilibrium relating to both isomorphous components were carried out by the method of isothermal supersaturation skimming in presence of vigorous mixing over a period of 4-5 hours. In the first series, we carried out a study of microconcentrations of each of the isomorphous components, using the radioactive indicators Zn^{65} and Cu^{64} respectively.

Experiments on the distribution of microconcentrations admixed with Zn, on crystallization of the double sulfate of copper and ammonia, were carried out in the following manner: into a concentrated solution of the copper salt was introduced the radioactive isotope Zn^{65}, in some cases admixed with ordinary zinc salts, then the process of crystallization was carried out. The original and the mother liquors and crystals were analyzed for copper salt content iodometrically and a measurement of the activity in solutions and crystals was obtained with reference to γ-radiated Zn^{65}. The specific activity of the solid phase was calculated according to the formula:

$$a'_{cr.} = a_{cr.} - \frac{(a_{liq.} - a_{cr.})\,(100 - c_{cr.})}{c_{cr.} \cdot c_{liq.}},$$

where: $a'_{cr.}$ is the activity of the solid phase (impulse per g.·min.),

$a_{cr.}$ is the activity of the wet crystals,

$a_{liq.}$ is the activity of the mother liquor,

$c_{cr.}$ is the content (in wt.%) of $CuSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ in the crystals,

$c_{liq.}$ is the content (in wt. %) of $CuSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ in the mother liquor.

The magnitude of the distribution coefficient when admixed with zinc on crystallization of the double copper salt was calculated according to the formula:

$$D^{*}_{(Zn)/Cu} = a'_{cr.} : \frac{a_{liq.}}{c_{liq.}}$$

The results of the experiments are given in Table 2.

TABLE 2

Zn content**	Temperature	Results of analytical determination of $CuSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (wt. %)			Impulses/g			$D_{(Zn)/Cu}$
		cryst.	mother liq.	orig. sol.	cryst.	mother liq.	sol. phase	
0.01	20°	94.73	22.73	25.17	113	21.5	227	2.39
0.01	20	95.00	22.87	25.47	111	21.4	226	2.41
0.01	20	93.10	22.73	25.47	273	27.2	297	2.48
0.10	20	91.82	22.71	27.68	166	18.0	183	2.31
0.10	20	91.68	22.67	27.68	217	22.0	240	2.48
0.10	25	94.90	24.91	28.92	148	15.8	157	2.47
0.10	25	91.71	25.06	28.92	176	20.0	196	2.45
1.00	20	82.30	22.20	27.02	160	18.4	202	2.43
1.00	20	84.45	22.12	27.02	196	22.6	239	2.35

**In the original solution, in % with reference to the basic solution (copper salts).

As seen from the data in this table, the magnitude of the equilibrium distribution coefficient with admixed Zn, with reference to its initial concentration, in a solution from ~ 0.01 to 1% (with respect to the hexahydrate salt) remains a constant value.

In a similar way, experiments were carried out on the correct explanation of the distribution of microconcentrations admixed with Cu, on crystallizing the double zinc salts using the radioactive isotope Cu^{64}. Measurements of the activity of solutions were also carried out with the γ-radiation of this isotope.

The zinc salts contained in the solutions and crystals were determined by titrating with potassium ferrocyanide using diphenylamine as indicator.

The results of the experiments are given in Table 3.

TABLE 3

Temperature	Results of analytical determination of $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (in wt. %)			No. of impulses/g			$D_{(Cu)/Zn}$
	in crystals	in mother liquor	in original solution	of crystals	of mother liquor	of solid phase	
20°	90.5	15.2	26.6	61.9	26.5	65.9	0.38
20	85.2	15.2	26.6	63.8	25.7	70.4	0.42
25	95.3	16.9	21.6	172	73.9	178	0.41
25	96.2	17.0	21.6	186	88.1	111	0.37

Note: The original solution contains admixed copper in an amount of 0.01% of the zinc content.

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*In characterizing D, the microcomponent is given in parentheses.

According to the data in this table, the magnitude of the distribution coefficient with admixed Cu, on crystallizing the double zinc salt, $D_{Cu/Zn}$, amounts to 0.40. In this way, two Khlopin constants (equilibrium distribution coefficients for microconcentrations of each of the isomorphous components), $D_{(Zn)/Cu}$ and $D_{(Cu)/Zn}$ are given side by side.

On the basis of this we can say that the system $CuSO_4 \cdot (NH_4)_2SO_4 - ZnSO_4 \cdot (NH_4)_2SO_4 - H_2O$ at 20° appears to be ideal in all ranges of concentration and that distribution of the components proceeds according to one general law both for micro- and macroconcentrations of both isomorphous components.

For additional confirmation of the correctness of this assumption, we carried out experiments on the distribution of isomorphous components at macroconcentrations in the liquid and solid phases. In these experiments, in order to attain equilibrium rapidly, with reference to both isomorphous components, the method of isothermal removal of supersaturation, with vigorous mixing, was also used. The original solutions, mother liquors and crystals, were analyzed for copper and zinc salt contents.

The copper content was determined by electroanalysis; after separating the copper, the zinc salt was determined in the solution by titrating with potassium ferrocyanide using ammonium molybdate as indicator (external).

In some of the tests, with reference to the initial materials used, the double salt of zinc ammonium sulfate, previously "contaminated" with the radioactive isotope Zn^{65}, on its recrystallization from aqueous solution, with a definite activity, was used. This permitted the possibility of analytical determination of the zinc salt and its replacement by measuring the activity of the mother liquor and crystals with subsequent conversion of the activity to the concentration of the zinc salt.

The results obtained are given in Table 4 and Figs. 1 and 2.

It is seen from the data given in Table 4, that the magnitude of the equilibrium distribution cofficient, $D_{Zn/Cu}$ or the reverse quantity $D_{Cu/Zn}$ is on an average a constant value for similar variations of related macroconcentrations of both components, this amount D being obtained in exactly the same way for microconcentrations of both components.

In this way we have established that the system

$$CuSO_4 \cdot (NH_4)_2SO_4 - ZnSO_4 \cdot (NH_4)_2SO_4 - H_2O$$

is ideal for all ranges of concentration of both isomorphous components. Accordingly the distribution curve in Fig. 2 is presented as a hyperbola [1].

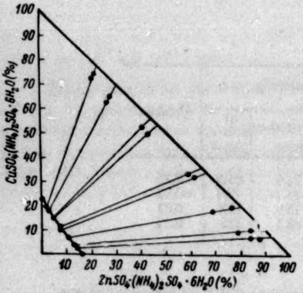

Fig. 1. Diagram of equilibrium compositions.

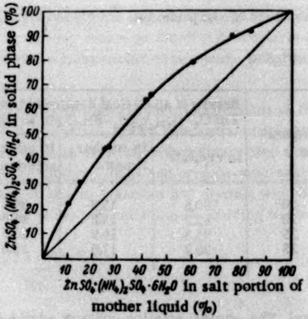

Fig. 2. Distribution diagram of components.

TABLE 4

Analytical results						Composition (%)					
crystals		mother liquor		original solutions		solid phase		salt portion of mother liquor			
$CuSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	$ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	$CuSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	$ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	$CuSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	$ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	$CuSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	$ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	$CuSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	$ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	$D_{Zn/Cu}$	$D_{Cu/Zn}$
74.16	21.0	19.55	2.22	23.57	3.95	77.73	22.27	89.56	10.44	2.46	0.41
73.36	20.3	18.97	2.18	23.57	3.95	78.05	21.95	89.69	10.31	2.44	0.41
65.13	27.4	17.37	3.08	23.21	5.82	70.07	29.93	84.94	15.06	2.41	0.41
62.84	27.0	17.55	3.22	23.21	5.82	69.44	30.56	84.50	15.50	2.39	0.42
52.36	40.6	14.86	5.07	18.65	9.59	55.79	44.21	74.56	25.44	2.32	0.43
50.10	42.7	14.50	5.06	18.65	9.59	53.57	46.43	74.13	25.87	2.48	0.40
32.43	59.2	10.76	7.76	12.82	12.98	34.80	65.20	58.10	41.90	2.58	0.39
30.25	61.5	10.04	7.40	12.82	12.98	32.37	67.63	57.57	42.43	2.84	0.35
19.90	76.5	6.90	10.0	8.03	16.44	20.48	79.52	40.80	59.20	2.56	0.39
18.35	69.1	6.89	10.4	8.03	16.44	20.40	79.60	39.79	60.21	2.56	0.39
10.54	84.0	3.87	12.5	4.50	20.05	11.03	88.97	23.57	76.43	2.50	0.40
9.14	80.0	3.80	12.7	4.50	20.05	9.93	90.07	23.03	76.97	2.78	0.36
7.84	87.6	2.78	13.5	3.35	21.18	8.13	91.87	17.42	82.88	2.32	0.43
8.06	83.7	2.82	13.4	3.35	21.18	8.65	91.35	17.35	82.65	2.22	0.45

SUMMARY

1. Experiments have been carried out on a study of the equilibrium distribution of components between the solid and liquid phases in the system

$$CuSO_4 \cdot (NH_4)_2SO_4 - ZnSO_4 \cdot (NH_4)_2SO_4 - H_2O$$

at 20 and 25° using the radioactive indicators Zn^{65} and Cu^{64}.

2. It has been established that the system is ideal at all ranges of concentration of both isomorphous components.

3. It has been found that the magnitude of the equilibrium distribution coefficient of zinc salts compared with copper salts $^{D}Zn/Cu$ is a constant both for microconcentrations and macroconcentrations of zinc salts and has an average value of 2.43. Accordingly, the reverse quantity, the equilibrium distribution coefficient of copper salts with reference to zinc salts, $^{D}Cu/Zn$ is shown to be constant for like corresponding components and is equal to 0.41.

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STUDY OF THE SYSTEM $(NH_4)_2BeF_4 - NH_4MnF_3 - H_2O$

L. R. Batsanova and A. V. Novoselova

From data in the literature, it is known that ammonium fluoroberyllate dissolves easily in water. Earlier, in a study of the system $NH_4F-BeF_2-H_2O$ [1], a solution of $(NH_4)_2BeF_4$, equivalent to 27.1%, was prepared at 0°. In contrast to ammonium fluoroberyllate, the manganese double fluoride, NH_4MnF_3 dissolves poorly in water. There are no definite data on the solubility of NH_4MnF_3; P. Nuka [2], gives an approximate figure for the solubility of this salt at 20° (1.2%). A study of the solubility diagram of the system $(NH_4)_2BeF_4-NH_4MnF_3-H_2O$ may be useful for locating the specific distribution of fluorine compounds of beryllium and manganese.

EXPERIMENTAL

For the work we synthesized ammonium fluoroberyllate and the double manganese fluoride. The salt $(NH_4)_2BeF_4$ was prepared by the reaction $Be(OH)_2 + 4HF + 2NH_4OH = (NH_4)_2BeF_4 + 4H_2O$.

Pure beryllium hydroxide was dissolved in the required amount of 40% hydrofluoric acid and to the solution obtained, a solution of ammonia was added. The solution containing ammonium fluoroberyllate was concentrated until crystallization started, then cooled to 0°. The crystals which separated were washed with ethyl alcohol and dried in the atmosphere.

The double fluoride of divalent manganese and ammonia was obtained by reacting solutions of manganese chloride and ammonium fluoride, in the form of finely crystalline, pale rose powder, which precipitated as a result of its low solubility. The salt, after separating, was washed with ethyl alcohol until free from chlorine ions and dried over P_2O_5.

Method and analysis. The study of the system $(NH_4)_2BeF_4-NH_4MnF_3-H_2O$ was carried out by the isothermal solution method. The experiments were carried out in a platinum crucible with a stirrer in a thermostat, at 25 ± 0.1°. The equilibrium which was established was controlled with respect to constancy of composition of the solution. For this, 10-20 hours was required. In control experiments, transference continued for 150-200 hours.

Samples of the saturated solution were withdrawn with a special steam-resistant pipette; the solution was filtered through a layer of cotton wool. The samples were weighed in platinum crucibles arranged in glass containers. The solid phase samples were removed with the aid of a heat-resistant small spoon, squeezed out slightly between sheets of filter paper, weighed and analyzed. The composition of the solutions was determined by analysis of the samples for manganese, beryllium and ammonium fluoride contents. Determinations of each of the components were carried out on a series of weighed portions. The concentration of ammonium fluoride was determined by driving off the ammonia from the alkaline solution. Estimation of beryllium fluoride content was carried out in the form of BeO after decomposition of the concentrated fluorides with sulfuric acid and precipitation of beryllium hydroxide.

In the selection of a method of determination of manganese, we decided on the polarographic method of analysis, which can be carried out quickly and with sufficient accuracy using small amounts of material (10^{-2} – 10^{-6} M.).

Polarographic estimation of manganese. Polarograms were taken in the automatic recording polarograph with galvanometer sensitivity $2.5 \cdot 10^{-9}$ a/mm/M. In work using a capillary with characteristics $m^{2/3} \cdot t^{1/6} = 2.24\ mg^{2/3} \cdot sec^{-1/2}$ [m is the weight of mercury which has flowed out of the capillary in 1 second (in mg), t is the time of formation of the drop (in seconds)]. Calculations of the strength of the diffusion current (in microamperes) were made according to the forlmula: $i_d = \frac{G \cdot H}{1/s \cdot l} \cdot 10^6$, where G is the absolute sensitivity of the galvanometer, H is the height of the polarographic wave (in mm), 1/s is the shunt coefficient of the galvanometer, l is the distance from the center of the galvanometer mirror to the scale.

With reference to the basis for the plotting of polarograms of solutions containing $(NH_4)_2BeF_4$ and NH_4MnF_3, a 0.5 N solution of ammonium fluoride was used. The polarographic wave of manganese was obtained on a 0.5 N solution of NH_4F, and was well defined, with a diffusion current proportional to the concentration of manganese. The relationship between the diffusion current and the concentration of manganese (within the range 0.3-1.4 m mol/liter) is given in Fig. 1.

Beryllium waves were not detected in the solutions containing ammonium fluoride. The presence of ammonium fluoroberyllate has no effect in practice on the height of the manganese wave; The values for the diffusion currents for manganese obtained for one and the same concentration of NH_4MnF_3, were the same in 0.5 N solutions of NH_4F and 0.2 N solutions of $(NH_4)_2BeF_4$. Samples of the solution under test containing the double fluoride of manganese and ammonium fluoroberyllate (0.5 g) were diluted to the required volume with a 0.5 N solution of ammonium fluoride; 10 ml of the solution obtained was placed in a polarographic cell, where two drops of 0.05% gelatine solution were added to depress the maximum. Dissolved oxygen was removed from the solution by passing in hydrogen for 20 minutes. The results of the determination of manganese by the polarographic method agreed with control data obtained by a chemical method (with the aid of hydroxylamine in the form of pyrophosphate). The accuracy of the polarographic measurement was 1-3%.

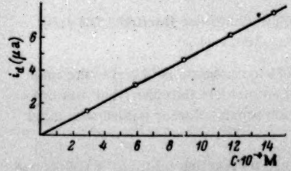

Fig. 1. Dependence of diffusion point on concentration of manganese in presence of 0.5 N NH_4F solution (calibrated directly).

The composition of the solid phases in the system was determined on many samples by the polarographic method, by the Shreinmaker residue method, and, apart from this, on all samples by crystal optics (by measuring the refraction of crystals by the immersion method).

For the determination of the composition of the solid phase, by the residue method, a sample was dissolved in a definite amount of water and measured portions of the solution removed for analysis for NH_4F, MnF_2 and BeF_2. As the system $(NH_4)_2BeF_4-NH_4MnF_3-H_2O$ appears in part as a quaternary system, and the fluorides of manganese, beryllium and ammonium contained in it may be expected to separate as double salts, the determination of the composition of the solid phases was carried out with reference to the quaternary system (in projections of the tetrahedral figure). By other methods, we concluded that the salts exhibited by the components of the systems studied, do not contain water. Graphical determination of the composition of the solid phases was difficult, since points corresponding to the composition of the solutions, and also of the precipitates, lay close to each other on the diagram owing to the low solubilities of the double manganese fluorides. Therefore, in all the experiments, apart from these, a crystal-optic investigation of the solid phases was carried out. First of all we recorded determinations of the refractive indices of the original substances NH_4MnF_3 and $(NH_4)_2BeF_4$. The determination of the refractive index of NH_4MnF_3 was difficult on account of the small particle size of the preparation. Crystals of NH_4MnF_3 on observation in crossed nichols, showed optical isotropism. It was not concluded, however, that the small figure for the double refraction (Ng − Nr) is covered by a low particle size of the preparation and the crystals appear to belong to the cubic system. Measurements of the refractive index of $(NH_4)_2BeF_4$ in view of its low order, were not possible with the aid of the immersion technique. Therefore, a series of low-refracting organic liquids with refractive indices in the range 1.33-1.40, was taken, this eliminating the use of the refractive index of $(NH_4)_2BeF_4$. The results obtained are given in Table 1.

Results of a study of the system $(NH_4)_2BeF_4-NH_4MnF_3-H_2O$ at 25°. A study of the solubilities in the system indicated was started with determinations of the solubilities of ammonium fluoroberyllate and the double manganese fluoride. As the investigation showed, the salt $(NH_4)_2BeF_4$ dissolves in water without decomposition. In the solid phase, it was found that ammonium fluoroberyllate was formed, substantially in equilibrium with the saturated solution, on investigation by precipitation and crystal optics methods. Its solubility at 25° is 32.3%.

TABLE 1

Refractive Indices of the Salts $(NH_4)_2BeF_4$ and NH_4MnF_3

Compound	Syngony	Shape of crystals	Optical sign	Refractive indices
$(NH_4)_2BeF_4$	Rhombic	Six-sided prisms	Negative	Ng 1.404 Nm 1.399 Nr 1.392
NH_4MnF_3	Tetrahedral	—	—	N 1.493

On studying the solubility of NH_4MnF_3, it was discovered that the double fluoride is slowly decomposed by water. On mixing solutions of the double fluoride of manganese and ammonia at 25°, the content of manganese fluoride in solution in the solid phase present remained constant for a period of 20 hours. On further mixing, the MnF_2 concentration in the solution began to go down gradually.

The measurement of the manganese fluoride concentration in a solution of the double fluoride, with reference to the time of mixing, is given in Table 2.

TABLE 2

Measurement of MnF_2 Concentration in a Solution of NH_4MnF_3 with Reference to Time of Mixing

Time of mixing (in hours)	MnF_2 in solution (%)	Time of mixing (in hours)	MnF_2 in solution (%)
10	0.96	130	0.71
20	0.96	150	0.70
40	0.92	170	0.70
50	0.92	200	0.70
60	0.88	210	0.68
70	0.79	230	0.68
100	0.75	250	0.68
110	0.71	290	0.66

After prolonged reaction with water (about 300 hours), the NH_4MnF_3 appears in the residue on roentgenographic and chemical analysis in presence of manganese fluoride. In solutions containing ammonium fluoroberyllate, there is no separation of NH_4MnF_3; we came to this conclusion owing to the constant composition of the solution over a period of 150 hours mixing.

The results obtained in a study of solubilities in the system $(NH_4)_2BeF_4-NH_4MnF_3-H_2O$ (25°) are given in Table 3.

As follows from the data in Table 3, on adding the double manganese fluoride to a saturated solution of $(NH_4)_2BeF_4$, the content of ammonium and beryllium fluorides in the solution is decreased considerably. The solid phase of these solutions (Experiments 1-4) represents ammonium fluoroberyllate. For a composition of the solution of 19.31% NH_4F, 12.31% BeF_2 and 0.26% MnF_2, the solution approaches saturation also with respect to NH_4MnF_3. We arrived at a solution of constant composition by adding ammonium fluoroberyllate to a saturated solution of the double manganese fluoride. Adding ammonium fluoroberyllate brings about a reduction in the MnF_2 concentration (Experiments 6-14). The solid phase in Experiments 6-14 represents the double manganese fluoride.

TABLE 3

Composition of Solutions Obtained on Reacting $(NH_4)_2BeF_4$ and NH_4MnF_3

Expt. No.	Composition (wt. %)				Mols/1000 mols water		Composition of solid phase
	NH_4F	BeF_2	MnF_2	H_2O	$(NH_4)_2BeF_4$	NH_4MnF_3	
1	19.72	12.58	—	67.70	70.72	—	$(NH_4)_2BeF_4$
2	19.66	12.49	0.12	67.73	70.45	0.34	
3	19.59	12.45	0.19	67.77	70.12	0.53	
4	19.47	12.40	0.25	67.88	69.47	0.71	
5	19.31	12.31	0.26	68.12	68.71	0.73	$(NH_4)_2BeF_4 + NH_4MnF_3$
6	15.66	9.94	0.29	74.11	51.07	0.72	NH_4MnF_3
7	11.57	7.32	0.37	80.74	34.31	0.88	
8	9.21	5.85	0.42	84.52	26.18	0.93	
9	7.98	5.01	0.46	86.55	21.83	1.02	
10	6.49	3.98	0.51	89.02	17.04	1.08	
11	5.11	3.15	0.54	91.20	13.17	1.12	
12	4.26	2.58	0.60	92.56	10.59	1.24	
13	2.35	1.35	0.66	95.64	5.34	1.31	
14	0.40	—	0.96	98.61	—	1.95	

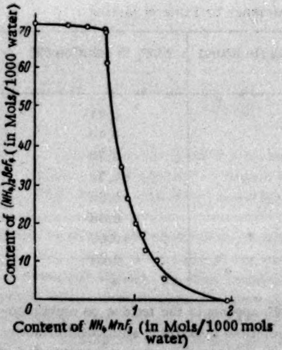

Fig. 2. Solubility isotherm of the system $(NH_4)_2BeF_4-NH_4MnF_3-H_2O$ at 25°

In Fig. 2 are illustrated the solubility isotherms of the system $(NH_4)_2BeF_4-NH_4MnF_3-H_2O$ (25°). In the diagram the abscissa represents the NH_4MnF_3 and the ordinate the $(NH_4)_2BeF_4$ content. In the graph the scale along the abscissa is divided into 25ths. The isotherm consists of 2 branches, corresponding to the solid phases NH_4MnF_3 and $(NH_4)_2BeF_4$. In this way the ammonium fluoroberyllate may be crystallized out from solutions containing the double manganese fluoride, NH_4MnF_3, as in the system $(NH_4)_2BeF_4-NH_4MnF_3-H_2O$ (25°) there are formed neither compounds between the components nor solid solutions.

SUMMARY

1. The solubility has been studied in the system $(NH_4)_2BeF_4-NH_4MnF_3-H_2O$ at 25°.

2. It has been shown that in the system there is neither formation of new compounds nor solid solutions. The basic phases of the system are represented by ammonium fluoroberyllate $(NH_4)_2BeF_4$ and the double manganese fluoride NH_4MnF_3.

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Moscow State University

STUDY OF THE METASTABLE EQUILIBRIA BETWEEN LIQUID PHASES. V

I. L. Krupatkin

In previous communications [1-4], ternary systems were described in which critical solution temperatures in the metastable state almost reached those for binary systems. Further study of metastable equilibria between liquid phases brought up the question of the possibility of realizing triple critical solution points in the metastable state and if possible, the principles of their formation. A solution of these problems is the object of the present work.

In selecting systems for study, we started from the fact described in previous communications, that ternary systems with metastable layer formation give similar types of equilibrium diagrams between the liquid phases as systems with stable layer formation. As a result of this, a ternary system of the layer formation type was sought on the basis of similarities found in ternary systems with upper triple critical points on the surfaces of the stable layer formation [5], with calculation of the special features of the form of equilibrium under investigation. In this way, a ternary system, in the binary part of which chemical compounds are formed, and in others (one or both), binary systems are realized by the phenomenon of metastable layer formation,and the desired form of diagram of state may be expected. With reference to such a system, the ternary system quinoline–diphenylamine–sulfur, was selected for study.

EXPERIMENTAL

For the work we took chemically pure diphenylamine, m. p. 54°, quinoline, purified by alkali and distilled off from the selected fraction, b. p. 237°; the sulfur had been recrystallized from benzene, m; p. 117° and therefore consisted of a mixture of the monoclinic and rhombic forms [6].

Of the binary systems, made up from the ternary system quinoline–diphenylamine–sulfur, the system sulfur–diphenylamine has already been described [5]. In it, below the crystallization curve for sulfur, there is a curve for equilibrium between the liquid phases, with an upper critical solution temperature of 104°, corresponding with a 32% diphenylamine content. Above the curve with layer formation there is a practically horizontal portion of the crystallization curve for sulfur at 105°. The system sulfur–quinoline has also been reported in the literature [7] and is similar to the previous system: in it the upper critical point corresponds to 102.5° and 26.5% quinoline content; the practically horizontal portion of the crystallization curve for sulfur is realized at 104.5°. The system diphenylamine–quinoline was investigated in the present work.

The system diphenylamine–quinoline was studied for fusibility and viscosity. Mixtures in this system form viscous and poorly crystalline solutions which do not fuse with diphenylamine. This investigation on fusibility was carried out by two parallel methods, the Shreder method [8] and the method of internal fusion. For carrying out the method, the ampoule containing the mixture was drawn out firmly to a tip, instead of being sealed. On shaking up the ampoule, the drop of mixture which had collected in it, froze. Throughout the period of cooling, the ampoule was vigorously shaken in order to distribute the liquid in contrast with the solidified clot, which played the part of a primer. The results obtained by both methods agreed within the limits of experimental error. The figures obtained for the material are given in Table 1 and the fusion curves are illustrated in Fig. 1, a. As seen from the data obtained, two compounds are formed between quinoline and diphenylamine, corresponding with the molecular proportions 1 : 1 and 5 : 3. The first of these melts congruently at 41.0° and contains 43.29% quinoline, the second compound melts at 37.0° incongruently and contains 55.99% quinoline; thus this latter melting point corresponds to the transition point E. The eutectic point found, e, corresponds to 32° and 25% quinoline. Mixtures with quinoline contents greater than 80% were not capable of crystallization.

TABLE 1

Equilibrium in the System Diphenylamine–Quinoline

Quinoline (wt. %)	Crystallization Temp., °C
0.00	54°
10.00	46
20.00	38
22.19	35
25.87	34
31.07	39
37.95	41
42.46	41
50.00	39
55.31	37
60.88	36
64.18	34
69.98	29
75.08	24
80.24	15

TABLE 2

Viscosity in the System Diphenylamine–Quinoline at 50°

Quinoline (wt. %)	Viscosity (centipoises)
20.79	5.848
30.96	5.676
40.00	5.521
43.28	5.470
45.00	5.203
46.67	4.902
50.00	4.558
54.00	4.561
56.12	4.558
60.39	4.145
65.00	3.610
70.17	3.199

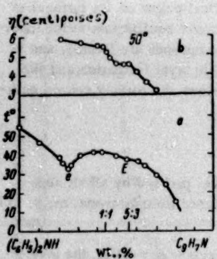

Fig. 1. Fusibility (a) and viscosity (b) in the system diphenylamine–quinoline.

A study of the viscosity was carried out in a capillary viscosimeter by the usual method [9]. The viscosity of the mixture was measured at 50°, i. e., on the one hand as near as possible to the melting points of the compoinds described and on the other hand at a sufficiently high temperature for crystallization of diphenylamine not to hinder the measurement at a high internal concentration. The figures obtained are given in Table 2 and the viscosity isotherms are represented in Fig. 1, b. As Fig. 1, b shows, there are two breaks in the viscosity isotherms, located between the viscosity values of the components; both these points correspond to the composition of compounds formed on fusion and their formation and presence are confirmed in the liquid phase.

The ternary system quinoline–diphenylamine–sulfur was investigated by the polythermal layer formation method of V. F. Alekseev [10] in sealed glass ampoules in an oil thermostat and partly by fusion. For this, sections were studied through the prism of the ternary system going from the sulfur edge to the side of the binary system quinoline–diphenylamine. In all, 8 such sections were studied, with quinoline contents of 20.0, 30.0, 40.0, 43.3, 50.0, 56.0, 60.0 and 80.0%. On studying the fusibility, it was found that with increasing quinoline content from section to section, and with increase in sulfur content in each section, crystallization became all the more difficult. In view of this, practically the complete sulfur crystallization curve was studied only in the first section with 20.0% quinoline; in the remaining sections, part of the sulfur crystallization curve, beginning at 40%, could not be obtained. Nevertheless, on accidental spontaneous crystallization of the compounds which separated, at a concentration interval of the layer formation, among them in each section were located mixtures which crystallized at much higher temperatures than the critical point of mixture in the liquid phase section. Crystallization of quinoline and diphenylamine in the ternary system was not studied. Figures relating to the sections are given in Table 3 and examples of the polytherms are illustrated in Fig. 2, where Fig. 2, a corresponds to the first section with a complete sulfur crystallization curve (Cr) and Fig. 2, b corresponds to the sixth section, a curve situated very high with layer formation.(Ra).

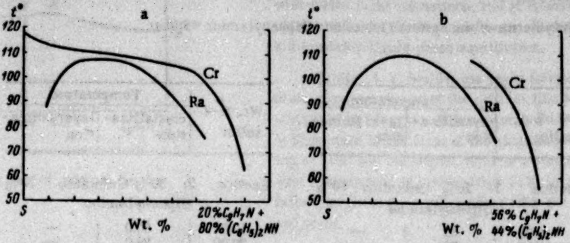

Fig. 2. Examples of polythermal sections of the prism of the system quinoline–diphenylamine–sulfur.

The results of the investigation show that the polytherms of the ternary system do not differ qualitatively from the polytherms of binary systems with layer formation. In a metastable liquid, the state of solubility of sulfur in mixtures of amines depends to an extent several times greater on temperature than the solubility of amines in sulfur; in this case, with increase in temperature the solubility of the liquid phase increases up to complete displacement. As a result of this the polythermal layer formation has maxima displaced to the sulfur side. The solubility of solid sulfur varies slightly with temperature at low temperatures up to 100-110°, the solubility temperature coefficient being markedly increased; therefore the crystallization curve has a very sloping part below the layer formation curve.

If a critical line is passed through the critical solution points of the binary system formed by sulfur and the maximal points of the polytherm of layer formation, then its projection to the edge of the binary system diphenylamine–quinoline will have the form represented in Fig. 3, curve K_1AKK_2. Beginning with the binary system sulfur–diphenylamine, the critical solution temperatures in the sections slowly increase up to the section with a composition of the compound with proportions 1 : 1 (point A). Beginning with this section, a rise in temperature takes place much more quickly and reaches a maximum figure of 109° in the section with composition of the compound, ratio 5 : 3 (point K) and then suddenly goes down. Already this variation in temperature shows that both compounds of the prevailing system diphenylamine–quinoline are reflected in the critical line and that on the surface of layer formation of the ternary system there is realized a singular line and an upper critical point.

With the polytherms obtained, the solubility isotherms of the solid and liquid phases of the ternary system quinoline–diphenylamine–sulfur were constructed and are illustrated in Fig. 4. In all, 6 isotherms with layer formation were constructed for 80, 90, 100, 105, 107 and 109°; they are shown in Fig. 4, a, from which it is seen that the surface of layer formation of the ternary system presents its own single surface linked with the surface of the ruptured solubility of the two binary layered systems. On this surface there is a synclinal singular edge corresponding to the binary system diphenylamine–quinoline and a compound with a molecular ratio of 1 : 1 with its own type of formation; for this, singular points were discovered on the enclosed isotherm of the layer formation.

Beginning at 104°, i. e., at the critical solution temperature, with the binary system sulfur–diphenylamine, the isotherms with layer formation are situated enclosed by the minima of the reciprocal solubilities of the liquid phases of sulfur admixed with amine and with two singular points; at the very highest temperatures, the isotherms decrease and at 109° are displaced to the upper triple critical point K. The latter rises not much above the rest of the surface; together with the minimum solubility it lies in the section corresponding to the binary system diphenylamine–quinoline, with a composition of the compound with a ratio of 5 : 3 and at the same time its formation is established at the minima shown. The upper triple critical point is situated at the composition 65.0% sulfur, 19.6% quinoline and 15.4% diphenylamine. The formation of this upper critical point is stipulated by the formation in the prevailing system diphenylamine–quinoline, of the chemical compound composition 5 : 3, with its organic solubility in the third component sulfur, and stable in the liquid phase to 109°. In this way the reasons for the formation of the upper triple critical points are the same for the stable and the metastable states.

TABLE 3

Polytherms of the System Quinoline–Diphenylamine–Sulfur

Wt. % of sulfur	Temperature	
	crystallization	layer formation
Section 1: 20% Quinoline 80% Diphenylamine		
9.99	65	—
20.07	90	—
30.03	102.5	82.0
40.02	104.5	92.0
50.00	106.5	102.0
55.07	107.5	104.5
58.04	108	106.0
60.00	—	107.0
69.99	—	107.0
80.01	—	105.5
90.03	—	92.0
Section 2: 30% Quinoline 70% Diphenylamine		
10.00	66.0	—
20.00	89.0	—
30.07	103.0	76
39.78	110.0	92
50.00	—	102
60.00	—	107
70.05	—	108
80.00	—	105
90.00	—	94
Section 3: 40% Quinoline 60% Diphenylamine		
9.90	65	—
20.23	90	—
29.99	104	74
39.73	112	90
52.24	—	103
60.00	—	107
70.04	—	108
79.97	—	105
89.99	—	89
Section 4: 43.3% Quinoline 56.7% Diphenylamine		
12.00	70	—
20.00	88	—
30.07	103	76
39.76	—	90.5
50.00	—	101.5
60.00	—	107
69.87	—	108
80.00	—	105
84.88	—	100
90.00	—	92
Section 5: 50% Quinoline 50% Diphenylamine		
10.01	63	—
20.27	89	—
30.11	103	79
41.23	—	94
50.00	—	103
60.05	—	109
70.09	—	109
80.00	—	106.5
90.07	—	93
Section 6: 56% Quinoline 44% Diphenylamine		
10.00	60	—
20.00	88	—
30.00	92	79
40.00	—	95
50.00	—	103
60.36	—	109
70.05	—	109
80.00	—	105
90.00	—	95
Section 7: 60% Quinoline 40% Diphenylamine		
10.76	68.5	—
19.66	89	—
25.06	97	—
30.21	101.5	78
39.82	—	92
47.63	—	101
59.59	—	108
70.52	—	108
80.06	—	105
90.13	—	93
Section 8: 80% Quinoline 20% Diphenylamine		
9.97	62	—
20.11	86	—
25.08	92	—
30.07	96	77
39.78	102.5	92
50.13	105	98
59.76	—	103
68.51	—	103
80.03	—	101.5
88.22	—	97

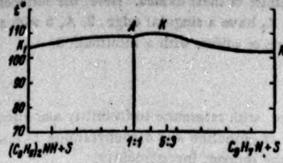

Fig. 3. Projection of critical line.

Nevertheless, the conditions for the formation of ternary systems of this type will differ from those for systems with stable layer formations; and it is necessary here, in order to have in the binary systems obtained (one or two) a metastable liquid phase equilibrium.

In Fig. 4, a, besides the layer formation isotherms, projections are shown of the critical line K_1AKK_2 for the composition triangle. In it a compound with the ratio 1:1 is illustrated in the form of the singular point A, corresponding to 108° and the higher point of a singular edge depicted with a compound of composition 5:3, in the form of an inflection point K, corresponding with the upper triple critical point.

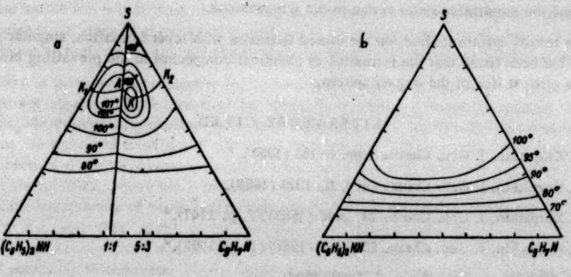

Fig. 4. Isotherms with layer formation (a) and crystallization (b) in the system quinoline–diphenylamine–sulfur.

In Fig. 4, b, the solubility isotherms are illustrated of solid sulfur in the system quinoline–diphenylamine–sulfur at 70, 80, 90, 95 and 100°. Each isotherm presents a minimum curve with a strongly diffused solubility minimum which is clearer with increasing temperature, when, at the same time the branch isotherms approach each other. This fact and the spontaneous crystallization of sulfur in the sections described above, illustrates the fact that the surface of crystallization of sulfur in the prism of the ternary system must have predominance, passing along the section through the sulfur edge between the edges of the two binary layer-formation systems. This result is brought about naturally and is in agreement with the relevant experimental facts. Actually, earlier [1], there was described the close relationship between metastable layer formation and crystallization and their mutual effect on each other. Externally this effect is shown by the fact that the curves and surfaces of layer formation and crystallization have a common course. Thus, if the surface of metastable layer formation has a saddle-shaped point, the surface of crystallization above it displays concavity.[3]. A similar effect of the common course is also displayed between the isotherms of stable layer formation and crystallization [11]. In this way it is natural that the presence in the ternary system in the metastable state, of upper critical points, corresponds to the concavity mentioned above, of the crystallization surfaces.

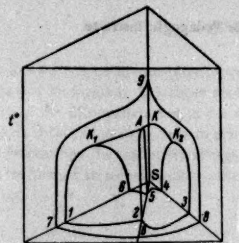

Fig. 5. General view of temperature-concentration prism of system quinoline–diphenylamine–sulfur.

The mutal arrangement of all the geometric elements of the diagram is seen in Fig. 5 where the usual qualitative forms of the temperature-concentration prisms of the system quinoline–diphenylamine–sulfur, are illustrated, components being denoted at the corners by the first letters of their names. Here, the surfaces of metastable equilibrium between the liquid phases 1, 3, 4, 6, K_1, K, K_2 have a singular edge, 2, A, 5 with a surface triple critical point K; 7, 8, 9 are the surfaces of crystallization of sulfur, with a minimum B.

SUMMARY

1. The binary system diphenylamine–quinoline has been studied, with reference to fusibility and viscosity. In it two chemical compounds are formed with molecular proportions of quinoline and diphenylamine 1:1 and 5:3 respectively; the first of these compounds melts congruently and the second, incongruently.

2. The ternary system diphenylamine–quinoline–sulfur has been studied with reference to layer formation, partly with reference to fusibility. In it the surface of the metastable layer formed has asynclinal singular edge and an upper triple critical point. The layer formation surface of the ternary system is linked with a flattening of the ruptured solubility of the two binary systems with layer formation.

3. It is explained that the formation of upper triple critical points on the surfaces of layer formation both for the stable and the metastable states is due to the same reasons.

4. In the ternary system studied, on the closed isotherms with layer formation, singular points were established. It has been found that the formation of chemical compounds in the prevailing binary system is reflected in the critical line of the ternary system.

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Cherkassy State Pedagogic Institute

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PHYSICOCHEMICAL STUDY OF THIOCYANATE COMPLEXES OF SILVER

A. M. Golub

Thiocyanate compounds resemble halides in many respects and therefore thiocyanate ions have come to bear the name pseudo-halides. On elucidating the general chemical properties of the thiocyanate ion, its resemblance to the halide ion is indicated in one of the basic properties, on comparing the capacity of these ions to form complexes. A study of thiocyanate complexes is of interest both from the practical point of view as well as with reference to their use in analysis and sometimes in the electrolytic separation of metals.

The chemistry of thiocyanate complexes begins its history with the first decades of the previous century. Silver thiocyanate was obtained for the first time by Porret [1] by means of an interchange reaction. With reference to the double thiocyanates of silver salts, their study was begun practically 100 years later. Gellwig [2] established first the increased solubility of AgCNS in thiocyanate solutions of the alkali metals. In 1902, Wells [3], on the basis of silver thiocyanate, isolated molecular compounds of three types, $Me_3Ag(CNS)_4$, $Me_2Ag(CNS)_3$ and $MeAg(CNS)_2$, where Me is the cation K^+ or Cs^+. There have also been indications of the existence of a double thiocyanate of composition $(NH_4)_5Ag(CNS)_8$ [4]. Foot [5], studying the double thiocyanates of silver, arrived at the result that, at 25°, of the complexes mentioned above, only the two latter were stable. The salt of composition $Me_3Ag(CNS)_4$ according to the data of this investigator, is easily decomposed to $Me_2Ag(CNS)_3$ and potassium thiocyanate. Foot's result was based on measurements of the heat of solution of complex salts and their components. Although crystals of the salt $Me_3Ag(CNS)_4$ decompose, in the case of a simpler constitution it may not be possible to demonstrate that corresponding complexes can be formed in solution, composed of 4 thiocyanate ions to 1 silver ion. Foot also studied the interaction of silver thiocyanate and potassium thiocyanate, determining the solubility of AgCNS in solutions of KCNS. Knowing the original amount of water, AgCNS, and KCNS, from the analytical data of the solution, he drew conclusions on the composition of the solid phase in equilibrium systems. From the results of his work, Foot concluded that the salt $K_3Ag(CNS)_4$ is not stable in the presence of heat and can only exist at low temperatures [6]. Ormont [7], speaking of the molecular silver thiocyanates, indicates only one of them, viz. $KAg(CNS)_2$. Many authors suggest that double thiocyanate complexes are only capable of formation in solution [4]. **Kirschner** [8] studied the solubility of AgCNS by measuring the emf of the substance:

$$Ag|0.1\,N\ AgNO_3|NH_4NO_3|0.1\,N\ KCNS,\ AgCNS|Ag,$$

at 18 and 25°. This investigator found that, with a 0.1 N solution of potassium thiocyanate only $Ag(CNS)_2^-$ groups can be formed. Krischner also showed that the amount of the complex is 300 times less than the concentration of the thiocyanate ion in the solution under test. With reference to the character of the formation of complex thiocyanates of silver in solution, the results of Randall and Halford attempted to deal with this and they determined the solubility of AgCNS in 0.312-1.124 M solutions of KCNS [9]. Assuming that $Ag(CNS)_2^-$ ions must be formed in solution, they attempted to calculate the equilibrium constant of the reaction:

$$AgCNS + CNS^- \rightleftarrows Ag(CNS)_2^-.$$

Since this amount has been shown to be variable for the KCNS concentrations investigated, the author came to the conclusion that the reaction proceeds more completely than might be expected in accordance with the equation indicated. In 1936, thiocyanate complexes of silver were studied by Ferrel, Ringion and Riley [10].

On the basis of potentiometric measurements, these authors calculated the solubility constants of the complexes, assuming different values for the coordination numbers. From the data obtained by them, there very probably existed a complex $Ag(CNS)_3^{-2}$. It is true that the authors did not deny the existence of simpler complexes of the group. Of recent investigations on the study of thiocyanate complexes of silver, there may be mentioned the work of Cave and Hume [11]. Cave and Hume measured the solubility of AgCNS in 0.005-2.252 M solutions of KCNS for solutions of constant ionic strength. Observing the variation in solubility of AgCNS with increased concentration of thiocyanate ions, the authors maintained that, in the solutions studied, three forms of complexes are produced, namely, $Ag(CNS)_2^-$, $Ag(CNS)_3^{-2}$ and $Ag(CNS)_4^{-3}$. The authors calculated the solubility product of AgCNS and the stability constants of the complexes. The results of Cave and Hume drew attention to themselves since they disagreed noticeably with the results of other investigators. The majority of authors who have studied the system $Ag^+-CNS^--H_2O$, indicate the instability of the simplest silver complexes. Cave and Hume assumed that the ions $Ag(CNS)_4^{-3}$ are already formed at thiocyanate-ion concentrations in the solution below 0.4 g-ion per liter. With reference to high concentrations of complex formation, these investigators speak of the probable formation of polynuclear complexes of the type $Ag_3(CNS)_6^{-3}$.

In this way the problem of the composition of thiocyanate complexes of silver in concentrated solutions of alkali metals, has not been solved completely. Also, the influence of temperature and nature of solvent is still vague. The present work was carried out with the object of filling the gap indicated.

Composition and Stability of Thiocyanate Complexes in Aqueous Solution

It is obvious that very complete determinations of the character of the reaction between silver ions and thiocyanate ions may be obtained only in a physicochemical study of equilibrium systems composed of the ions indicated and solvents in which complex formation is produced. In this way the dependence of the complex formation on different external conditions may be traced and a qualtitative determination made.

A study of thiocyanate complexes of silver was carried out by us by two methods, potentiometrically and by the method of solubility determination. The measurement of the potential of the silver electrode and also the determination of the solubility of AgCNS in medium and high concentration fields of complex formation was carried out by us for constant ionic strength of the solutions. For this, we introduced into the solutions studied, potassium nitrate, in such an amount that the molar sum of KCNS and KNO_3 in all cases was exactly the same. In the potentiometric measurements, we started with solutions of $AgNO_3$, the concentration of which was constant (0.01 M), in the mixtures investigated. The KCNS concentration varied from 0.6 to 1.8 M. For the preparation of the initial solutions, KCNS, chemically pure grade and previously recrystallized, was used. The carefully dried salt was melted gently for 5-10 minutes, in order to remove occluded moisture [12]. After cooling off, the amount of salt required for the preparation of the solution was weighed out on analytical balances. The salts $AgNO_3$ and KNO_3, used in the work, were the chemically pure grade.

The ranges investigated had the following form:

$$\begin{array}{lllll} Ag \mid AgNO_3, & KCNS, & KNO_3 \mid & KNO_3 \mid & KCl,\ Hg_2Cl_2 \mid Hg. \\ 0.01\ M & x\ M & (1.8-x)\ M & Dry & Dry \end{array}$$

The measurements of emf were carried out by the compensated method in a type PPTV-1 potentiometer with the aid of a mirror galvanometer GEP-47.

Each substance was kept in a thermostat until a significant resistance of the electrode potential could no longer be detected.

All the calculations were carried out in exactly the same way as for the study of iodide complexes of silver [13]. The composition of the complexes in solution was determined from the tangent of the angle of slope of the straight line, expresses by the relationship:

$$\log \frac{[Ag(CNS)_m^{1-m}]}{[Ag^+]} = m\log[CNS^-] - \log K.$$

The results of our measurements at 20° are given in Fig. 1 and Table 1.

TABLE 1

KCNS concentration (M)	log[KCNS]	E_{Ag/Ag^+} (V)	$\log \frac{[Ag(CNS)_m^{1-m}]}{[Ag^+]}$	$K_4 = \frac{[Ag^+][CNS^-]^4}{[Ag(CNS)_4^{-3}]} \cdot 10^{11}$
—	—	+0.4155		
0.6	−0.2218	−0.1426	9.6110	2.41
0.8	−0.0969	−0.1686	10.0602	2.90
1.2	+0.0792	−0.2115	10.7970	2.59
1.4	+0.1461	−0.2272	11.0689	2.92
1.6	+0.2041	−0.2427	11.3339	2.75
1.8	+0.2553	−0.2520	11.4940	3.08
2.1758	+0.3377	−0.2717	11.8348	3.04

Note: 1. In all the results the coordination number m = 4.
2. Values for the potentials are given against a saturated calomel electrode.

As seen from Fig. 1, the inclination of the straight line to the axis log[CNS⁻] indicates the formation of a complex with coordination number m = 4. In the last column of Table 1 the values for dissociation constants of $Ag(CNS)_4^{-3}$ complexes are given, calculated according to the formula

$$K_4 = \frac{[Ag^+]\left([KCNS]_{tot.} - 4\,[Ag(CNS)_4]\right)^4}{[Ag]_{tot.} - [Ag^+]}.$$

In previous investigations of KCNS concentration, we found the figure of $2.86 \cdot 10^{-11}$ for the dissociation constant of $Ag(CNS)_4^{-3}$. This value is 2.5 times less than that obtained by Cave and Hume [11]. It is true that the investigations mentioned were carried out at 25° and not at 20°.

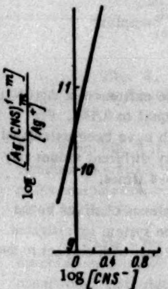

Fig. 1. Study of the system $Ag^+ - CNS - H_2O$ at 20°.

The composition of the thiocyanate complex of silver was also determined at 20° by the solubility method. For this, a series of KCNS solutions were prepared from 0.1 to 1.0 M. Into these solutions dry AgCNS was introduced until saturated. We obtained silver thiocyanate by mixing solutions of $AgNO_3$ and KCNS. The precipitated AgCNS, after filtration and careful washing, was dried in a desiccator over calcium chloride. The reaction mixtures were kept in closed flasks for about two days with frequent shaking. Dissolution of silver thiocyanate in these proceeded according to the equation:

$$\underset{\text{solid}}{AgCNS} + nCNS^- \rightleftarrows Ag(CNS)_{n+1}^{-n}. \qquad \text{(I)}$$

From the quantitative point of view, this reaction is characterized by constant equilibrium;

$$K_s = \frac{[Ag(CNS)_{n+1}^{-n}]}{[CNS^-]^n},$$

or, in the polarographic form

$$\log [Ag(CNS)_{n+1}^{-n}] = \log[CNS^-] - n\log K_s,$$

where the angle coefficient n, for existence of one of the complexes in a given interval of concentration of complex formation, has one definite value.

In the graphical representation there is just as much dependence; instead of the concentration of free CNS^- ions, the total potassium thiocyanate concentration in the system studied may be taken, since the difference between their polarograms is very small.

The concentration of $Ag(CNS)_{n+1}^{-n}$ ions was determined from the amount of silver found in equilibrium solutions. Ag was determined gravimetrically by precipitating with carbon disulfide. Ag_2S precipitates, after weighing, were carefully washed, first with water, then alcohol, ether, carbon disulfide, then again with alcohol and ether and dried at 90°.

The results obtained are given in Table 2 and Fig. 2.

The solubility method permits us to obtain results on the predominant formation of $Ag(CNS)_4^{-3}$ complexes in solutions with a sufficiently large excess of thiocyanate ions. The equilibrium constants were calculated on the basis of the solubility data:

$$K_s = \frac{[Ag(CNS)_4^{-3}]}{([KCNS]_{tot.} - 3[Ag(CNS)_4^{-3}])^3}.$$

TABLE 2

KCNS concentration (M)	log [KCNS]	Wt. Ag_2S per 40 ml sol.	$\log[Ag(CNS)_{n+1}^{-n}]$	$K_{s.} = \frac{[Ag(CNS)_4^{-3}]}{[CNS^-]^3}$	$K'_{s.} = \frac{[Ag(CNS)_3^{-2}]}{[CNS^-]^2}$
1.0	0	0.3760	−1.1153	0.160	0.102
0.7	−0.1549	0.1616	−1.4867	0.150	0.081
0.6	−0.2218	0.1054	−1.6723	0.138	0.068
0.5	−0.3010	0.0648	−1.8836	0.134	0.058
0.3	−0.5229	0.0160	−2.4910	0.132	0.037
0.2	−0.6990	0.0056	−2.9469	0.149	0.029

Note: From the slope of the line, (Fig. 2) within the limits of concentration of complex formation studied, the slope coefficient n = 3.

Completely satisfactory constancy of this constant also indicates the benefit of the existence of $Ag(CNS)_4^{-3}$ groups under the given conditions. The average value for the equilibrium constant is equal to 0.145. For comparison, the values are also given in Table 2, of the equilibrium constants K'_s which have been calculated allowing for the formation of $Ag(CNS)_3^{-2}$ complexes. Then, as in the first case, two very different values vary by less than 1.5 times, for K'_s the extreme values in the series exceed one another by 3-4 times.

On the basis of the data obtained in a study of the formation of thiocyanate complexes of silver by the solubility method, apart from $Ag(CNS)_4^{-3}$, there are formed simultaneously with it, in the system investigated, more simple groups than the large ones and in this case the large excessof thiocyanate ions, with respect to the silver taken, was not attained.

Using the values K_s and K_4 which were obtained, we also calculated the solubility product (SP) of AgCNS. For this, the SP of the salt was determined repeatedly, the values found varying within the limits $1.14 \cdot 10^{-12}$ to $6.8 \cdot 10^{-13}$ [7]. Cave and Hume found a figure for the SP equal to $6.75 \cdot 10^{-12}$

If the expression for the constant $K_4 = \frac{[Ag^+][CNS^-]^4}{[Ag(CNS)_4^{-3}]}$ and $K_s = \frac{[Ag(CNS)_4^{-3}]}{[CNS^-]^3}$ transposing

we obtain

$$K_1 \cdot K_s = [Ag^+][CNS^-] = SP.$$

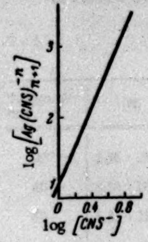

Fig. 2. Study of the system AgCNS – KCNS – H_2O by the solubility method.

It follows that the SP of AgCNS is equal to $4.14 \cdot 10^{-12}$. **Our value was ~ 4 times greater than the very high values cited elsewhere but 1.5 times less than the value obtained by Cave and Hume [11].**

The Influence of Temperature on Thiocyanate Complexes of Silver in Solution

As already discussed, some authors have stated that $Ag(CNS)_4^{-3}$, on account of its low thermal stability at room temperature would not be formed [4]. However, such a result, as we have already shown, does not correspond to the facts. In order to obtain a more complete characterization of the thermal stability of the $Ag(CNS)_4^{-3}$ complex, we carried out potentiometric measurements in the system $Ag^+ - CNS^- - H_2O$ at 20, 40 and 60°.

The data for the potentiometric measurements at 40 and 60° are seen respectively in Tables 3 and 4. The composition of the complexes in these cases was also determined by a graphical method (Figs. 3 and 4).

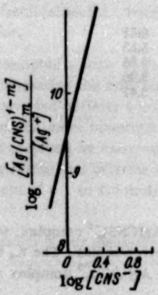

Fig. 3. Study of the system $Ag^+ - CNS^- - H_2O$ at 40°.

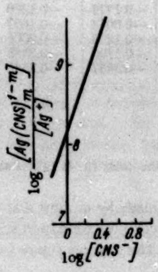

Fig. 4. Study of the system $Ag^+ - CNS^- - H_2O$ at 60°.

From Fig. 3 it is easily established that at 40°, as well as at 20° in the field of high concentrations of complex formation, mainly $Ag(CNS)_4^{-3}$ complexes are formed. This is also indicated by the fairly good stability of the dissociation constant of this complex in a broad concentration interval of CNS ions (Table 3). The average value for the dissociation constant at 40° is equal to $3.56 \cdot 10^{-10}$.

In Table 4 the results are given of a study of our system at 60°. In the last column here the values for the dissociation constant of $Ag(CNS)_3^{-2}$ are given side by side with $Ag(CNS)_4^{-3}$ in the quantity foumed under the given conditions. Calculated according to the slope of the straight line

$$\log \frac{[Ag(CNS)_m^{1-m}]}{[Ag^+]} = m\log[CNS^-] - \log K,$$

the coefficient m = 3.4 and not 4 as is the case for 20 and 40°.

TABLE 3

KCNS concentration (M)	log[KCNS]	E_{Ag/Ag^+} (V)	$\log \frac{[Ag(CNS)_m^{1-m}]}{[Ag^+]}$	$K_4 \cdot 10^9$
—	—	+0.4033		
0.6	−0.2218	−0.1267	8.5346	2.87
0.8	−0.0969	−0.1566	9.0161	3.22
1.2	+0.0792	−0.1986	9.6924	3.68
1.4	+0.1461	−0.2145	9.9485	3.85
1.5509	+0.1906	−0.2255	10.1256	3.90
1.7725	+0.2187	−0.2407	10.3701	3.84

Note: In all the results, m = 4.

TABLE 4

KCNS concentration (M)	log[KCNS]	E_{Ag/Ag^+} (V)	$\log \frac{[Ag(CNS]_m^{1-m}]}{[Ag^+]}$	$K_4 \cdot 10^9$	$K_3 \cdot 10^9$
—		+0.3887			
0.6647	−0.1773	−0.1280	7.5750	4.05	6.81
0.9970	−0.0013	−0.1697	8.2057	5.22	5.63
1.3295	+0.1235	−0.2006	8.6732	5.87	4.66
1.5509	+0.1906	−0.2188	8.9486	5.87	3.96
1.7725	+0.2487	−0.2348	9.1906	5.81	3.41

Note: In all the tests m is taken as equal to 3 and 4.

The calculations made by us show that the dissociation constant of the $Ag(CNS)_3^{-2}$ complex, within the concentration limits of complex formation studied, have not very greatly different values. The K_4 values maintain a good constancy. The average figure for the dissociation constant of the $Ag(CNS)_4^{-3}$ complex at 60° is equal to $5.36 \cdot 10^{-9}$.

A comparison of the dissociation constants of the $Ag(CNS)_4^{-3}$ complex, calculated for different temperatures, shows that, with increase in temperature, the stability of the complex falls. Therefore, the process of formation of complex ions in the case quoted must proceed exothermically.

$$Ag^+ + 4CNS^- \rightleftarrows Ag(CNS)_4^{-3} + Q. \tag{II}$$

We made a calculation of the heat of the reaction of formation of the thiocyanate complex of silver in accordance with equation (II). For this, the Van't Hoff isochore relationship was used:

$$\frac{d \ln K}{dT} = -\frac{Q}{RT^2}.$$

It is satisfactory to use the isochore relationship directly in the interval form in which the natural logarithms have been converted to the base 10:

$$\log \frac{K_2}{K_1} = \frac{Q(T_2 - T_1)}{4.575 \cdot T_1 \cdot T_2}.$$

With the use of this relationship it is possible to estimate the thermochemical effect, obtaining measurements at low temperature intervals [14].

In Table 5 the values are given for the heat effect of the $Ag(CNS)_4^{-3}$ formation reaction.

TABLE 5

Temperature	K_4	Q(kcal)
20°	$2.86 \cdot 10^{-11}$	22.97
40	$3.56 \cdot 10^{-10}$	28.08
60	$5.36 \cdot 10^{-9}$	

The average value for the heat of formation of $Ag(CNS)_4^{-3}$ within the temperature range 20-60°, is approximately equal to 25.5 kcal. It follows that the formation of the silver thiocyanate complex in solution has the character of an exothermic reaction. As seen from Table 5, with increasing temperature the heat effect of the complex-formation reaction increases slightly.

The Influence of the Nature of the Solvent on the Formation of Thiocyanate Complexes of Silver

It is known that the values for the electrode potentials of metals depend on the nature of the solvent with which the metals cited are in equilibrium [15]. The presence of ion-complex-formers which are capable of linking up into more or less stable complexes of ions with definite potentials [12], also has an important effect on the value of the electrode potential. This latter factor acts at an important stage on the order of distribution of metals in the electrochemical series. Therefore, it is of interest to find out to what extent the complex formation depends on the solvent.

We attempted a study of the course of the complex formation reaction in relationship to the nature of the solvent, by measuring the emf and by the solubility method. Potentiometric measurements were carried out as indicated above but definite amounts of non-aqueous solvents — ethyl alcohol, acetone or dioxane, were introduced into the solutions under investigation. The solvents were carefully distilled and dehydrated. The solutions investigated were prepared by carrying out a definite series of tests, the concentration of the non-aqueous solvent being kept constant and only the concentration of the complex-former being varied. Solutions with a non-aqueous solvent content of 0.1 to 1.2 mol/liter were studied by the emf method. The measurements were carried out at 20°.

The results of our measurements are given in Table 6, for solvent mixtures with a dioxane concentration of about 1 M.

TABLE 6

KCNS concentration (M)	log[KCNS]	$^{-}E_{Ag/Ag^{+}}$ (V)	$\log \frac{\left[Ag(CNS)_m^{1-m}\right]}{[Ag^{+}]}$	$K_4 \cdot 10^{11}$
—	—	+0.4147	—	
0.4	—0.3979	—0.1029	8.9105	2.06
0.6	—0.2218	—0.1425	9.5921	2.52
0.8	—0.0969	—0.1706	10.0757	2.80
1.2	+0.0792	—0.2122	10.7918	2.92
1.8	+0.2553	—0.2550	11.5284	2.84

Note: In all the tests m = 4.

We were limited to a show of data relating to solutions containing dioxane since dioxane has very little effect on the dielectric permeability (DP), compared with other solvents studied by us and would show a very much greater effect on the electrode potential and on the complex formation.

However, as seen from Table 6, the values for the silver electrode potential and the $Ag(CNS)_4^{-3}$ dissociation constant for dioxane solution do not differ at all markedly from the values found for pure aqueous solutions (see Table 1). We also noticed this on replacing water in aqueous-alcohol and aqueous-acetone mixtures.*

At the same time we saw that even an insignificant change in the thiocyanate ion concentration brings about a marked reduction in the electrode potential figure both in the presence of non-aqueous solvents and in pure aqueous solutions.

We used the solubility method for the study of complex formation in pure non-aqueous solvents; for this acetone and alcohol solutions were obtained. KCNS is not soluble in dioxane. Potassium thiocyanate dissolves with difficulty in anhydrous ethyl alcohol; a saturated solution at 20° contains 0.5326 mol/liter KCNS. The AgCNS solubility in alcoholic KCNS solutions is also not very high. We found that the AgCNS concentration in a saturated KCNS solution at 20° reaches 0.00166 mol/liter. This is a very low AgCNS solubility for the corresponding KCNS concentration, in aqueous solution, Therefore we can say that the stability of the silver thiocyanate complex is higher in water than alcohol.

The formation of the thiocyanate complex of silver proceeds much more easily in acetone than in alcohol and water. AgCNS is practically insoluble in pure acetone and therefore the solution shows complex formation activity in presence of KCNS.

We studied the equilibria in the system AgCNS − KCNS in acetone solution by the method described for aqueous solutions. The KCNS concentration varied from 0.1 to 1 M. The results obtained are given in Table 7.

The value n was determined graphically (Fig. 5) and is equal to unity. It follows that the composition of a thiocyanate complex of silver formed in acetone solution corresponds to the formula $Ag(CNS)_2^{-1}$. We arrived at this result and calculated the equilibrium constant $K_s = \frac{[Ag(CNS)_2^-]}{[CNS]}$ (average value 0.404) which shows a much better constancy than

$$K'_s = \frac{[Ag(CNS)_3^{-2}]}{[CNS^-]^2} \text{ or } K''_s = \frac{[Ag(CNS)_4^{-3}]}{[CNS^-]^3}.$$

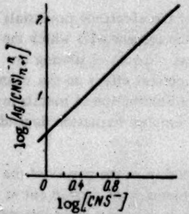

Fig. 5. Study of the system $AgCNS - KCNS - CH_3COCH_3$ by the solubility method.

TABLE 7

KCNS concentration (M)	log [KCNS]	Wt. Ag_2S per per 20 ml sol.	$\log[Ag(CNS)_{n+1}^{n}]$	K_s	K'_s	K''_s
1	+0.0	0.7264	−0.5331	0.4147	1.723	166.7
0.8	−0.0969	0.5996	−0.6163	0.4235	2.407	588.8
0.6	−0.2218	0.4108	−0.7805	0.3820	2.30	153.5
0.4	−0.3979	0.2827	−0.9428	0.3987	3.856	593.3
0.2	−0.699	0.1431	−1.2385	0.4018	6.460	196.0

Note: In all the experiments n = 1.

From the acetone solution we produced crystallization of the compound formed in it. Thanks to the high flexibility of the solvent pair at room temperature, concentration of the acetone solution of the mixed thiocyanates of silver and potassium proceeds very rapidly. As a result of isothermal crystallization, we obtained separation of a more silky substance in the form of needle-shaped crystals. For this we prepared an acetone solution of approximately 0.8 M KCNS concentration and saturated it with respect to AgCNS then left it to stand in a desiccator over calcium chloride at room temperature. After 3 days, formation of a precipitate was observed; this was rapidly separated from the mother liquor, washed twice with anhydrous acetone, dried in a desiccator and analyzed for potassium and silver. The difference between the weighed portion and the amounts calculated according to the analytical data for KCNS and AgCNS, gave the acetone content of the crystals. In the results it was established that the molecular compound which separated corresponded to the formula

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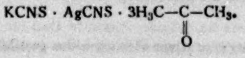
*Here, it is true, in contrast to pure aqueous solutions, the solution of the AgCNS precipitate approached the KCNS at somewhat lower concentrations.



$$KCNS \cdot AgCNS \cdot 3H_3C{-}\underset{\overset{\|}{O}}{C}{-}CH_3.$$

Theoretically, this compound should contain: 22.37% KCNS, 37.97% AgCNS and 39.66% acetone.

According to the analytical data, there was found: 37.10% acetone 24.23% KCNS and 38.67% AgCNS. The molecular compound which separated is easily decomposed by water and rapidly effloresces in the atmosphere losing acetone of crystallization.

DISCUSSION OF RESULTS

Dissociation constants of thiocyanate complexes of silver were calculated on the basis of potentiometric measurments at different temperatures and undoubtedly show that the process of complex formation in a given system depends largely on temperature. With increasing temperature, the stability of complexes diminishes.

However, $Ag(CNS)_4^{-3}$ formation under conditions of a large excess of CNS^- ions in aqueous solution, prevails up to 60°. Our results refute the results given by other investigators who have pointed out the high thermal instability of quaternary thiocyanate complexes of silver. As we have established, $Ag(CNS)_4^{-3}$ only begins to partially dissociate at 60° according to the equation:

$$Ag(CNS)_4^{-3} = Ag(CNS)_3^{-2} + CNS^- \qquad \text{(III)}$$

It may be assumed that at higher temperatures dissociation of the silver thiocyanate complex proceeds further. It follows that gradual dissociation concerns not only the slightly stable but also the stable complexes such as silver thiocyanates.

The nature of the solvent has a no less powerful effect on complex formation, for which there is interaction between Ag^+ and CNS^- ions.

In aqueous solution $Ag(CNS)_4^{-3}$ groups prevail, in acetone $Ag(CNS)_2^-$ groups. A comparison of the equilibrium constants permits us to conclude that complex formation proceeds easily in acetone, is worse in water and still worse in alcohol.

The fact that the stability of the complexes in acetone is much higher than in water is shown by adding small amounts of water to an acetone solution containing thiocyanate complexes, when at once a white turbidity of AgCNS begins to appear. The latter test indicates the powerful dissociating properties of water with respect to thiocyanate complexes of silver. Thus, in mixed solvents (water – acetone, water–dioxane, water – alcohol) with a sufficiently high concentration of non-aqueous solvent, the dissociation constants of the complexes and their composition hardly vary at all from those given in pure aqueous solutions.

Our experiments also show that the dependence of complex formation on solvent is not linked in any simple way with dielectric permeability (DP) of the solvent. The very high DP of water (81 7), less for alcohol (25.8) and still less for acetone (20.7) are known. The capacity for formation of thiocyanate complexes of silver in these solvents varies in the ideal state in series. If the DP of the solvent were a decisive factor in complex formation in solution, we should expect an increase in the equilibrium constant (I) from water to alcohol.

The effect of the solvent on complex formation is the more powerful if we attribute to it not only a variation in stability and composition of the complexes in solution, but the character of the separation of molecular compounds in the solid form. Then, from aqueous solutions, double thiocyanates of potassium and silver would be produced only in the form of anhydrous crystals precipitated from acetone.

The data obtained by us offer the possibility of results which depend on the method of production, composition of thiocyanate complexes of silver formed being different, in spite of concentration conditions being kept the same in different cases. The obtaining of emf values by us for aqueous and mixed solutions shows that in the system $Ag^+ - CNS^-$ – solvent complex formation has more effect on the value of the equilibrium electrode potential than the nature of the solvent. In spite of fairly high concentrations of non-aqueous solvents in systems studied, the electrode potential values are practically the same as for aqueous solutions if conditions are not varied.

A study of thiocyanate complexes of silver also gives the possibility of more complex characterization of the chemical individuality of the thiocyanate ion. As already mentioned, the CNS^- approximates closely to the halogen ion in properties. With reference to this, in order to place CNS^- in the halogen series according to its capacity for forming silver complexes, we have compared the values for the dissociation constants of AgX_4^{-3} complexes, where X^- is Br^-, I^- and CNS^- ion. At 20-25° for the bromide complex $K = 7.14 \cdot 10^{-10}$ [16] and for the iodide complex, $K = 1.8 \cdot 10^{-14}$ [13]. On comparing these constants with the dissociation constants of silver thiocyanate at 20°, found by us, we obtain the following series:

$$Cl^- < Br^- < CNS^- < I^-.$$

However, this series cannot be calculated absolutely since the nature of complex formation often depends very much on the nature of the central ion.

In the series the thiocyanate ions are very similar and differ essentially from Br^- and I^- anions. When the latter ions form complexes of the type AgX_3^{-2} [13, 17] in the field of high concentrations, with the silver cations in aqueous solutions, the thiocyanate complex under similar conditions has a coordination number of 4. We may also add that there is a considerable difference between CNS^- and I^- ions with reference to their capacity for forming complexes in acetone solution. In this case the iodide complex corresponds to the formula $Ag_3I_4^-$ [16] and the thiocyanate forms groups of composition $Ag(CNS)_2^-$.

SUMMARY

1. The formation of thiocyanate complexes of silver in aqueous and non-aqueous solvents has been studied potentiometrically and by the solubility method.

2. It has been shown that in aqueous solutions in the field of medium and high KCNS concentrations, the complexes $Ag(CNS)_4^{-3}$ are formed predominately.

3. The dissociation constants of $Ag(CNS)_4^{-3}$ have been calculated at 20, 40 and 60° and also the heat effect has been found for the silver thiocyanate complex. It has been shown that with increasing temperature, the stability goes down and the composition of the complex is simplified.

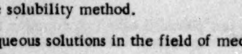
4. The equilibrium constants at 25° have been calculated.

$$\underset{\text{solid}}{AgCNS} + nCNS^- \rightleftarrows Ag(CNS)_{n+1}^{-n}$$

for aqueous and acetone solutions and also the AgCNS solubility in aqueous solutions has been obtained.

5. With reference to the capacity for formation of thiocyanate complexes of silver, acetone occupies first place, water comes next and finally alcohol. In mixed aqueous – non-aqueous solvents up to 1.2 M concentration, with non-aqueous additions the dissociation constants of complexes and their composition have the same values as for aqueous solutions.

6. It has been shown that in acetone solution, in contrast to aqueous, the complex $Ag(CNS)_2^-$ is formed. The molecular compound was isolated:



$$KCNS \cdot AgCNS \cdot 3H_3C-\underset{\overset{\|}{O}}{C}-CH_3$$

7. It has been shown that thiocyanates and halides are arranged in the following series, according to their capacity for forming complexes with silver

$$Cl^- < Br^- < CNS^- < I^-.$$

8. On the basis of the experimental data obtained, conclusions are drawn on the comparative effect of nature of the solvent and complex formation on the equilibrium electrode potential values.

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THE ROLE OF pH IN THE FORMATION AND EXTRACTION OF INTERNAL COMPLEX COMPOUNDS

I. M. Korenman and F. R. Sheyanova

The role of pH in the formation of internal complex salts has been repeatedly mentioned in the literature and is of high significance inpractice. . Of the well known examples we may mention the formation of hydroxyquinolates [1-6], anthranilates [7, 8], dithizonates [2-4] and other compounds[9-13] the yields of which have undergone sudden fluctuation in relationship to pH. A. K. Babko [14, 25] and V. I. Kuznetsov [15, 26], devoted special investigations to the dependence of the color of internal complex salts on pH. The work of a series of authors has shown that the formation of internal complex salts was begun with the determination of pH value; with increase in pH, the yield of reaction product is increased and finally, reaches 100%. However, a further increase in pH produces a more or less considerable lowering of the yield of reaction product and the reaction may even cease completely. A series of such examples is mentioned by V. I. Kuznetsov [13, 15, 16]. R. Berg [1] and S. A. Voznesensky [17] produced graphs of the precipitation of some hydroxyquinolates with reference to dependence on pH which had the characteristic form of graphical recordings of the effect of pH. A similar picture is seen in the varying amounts of dithizonates extracted [2, 18, 19], hydroxyquinolates [20, 21] and other compounds [22-24], at different pH values.

This effect has been little discussed. V. I. Kuznetsov says that increased intensity of color of complex tartrate compounds, at high pH, is not linked with their complete destruction since hydroxides do not separate out, although the colors observed are reminiscent of those of corresponding hydroxides.

Pyrocatechol complex compounds of iron, in presence of a large amount of caustic alkali, suddenly decrease in color intensity the color in this case being nearer to that of an iron hydroxide suspension. In some cases, separation of the corresponding hydroxide [13, 15] is noticed by the action of excess alkali on the internal complex compound. A. K. Babko [14, 25], indicates that on decomposition of complex compounds hydroxides are formed. Formation of hydroxides or basic salts at high pH values is not always observed visually. This may often be explained by the small amount of hydroxide present, as a result of the low concentration, or also by the colloidal state of the hydroxide.

It may be suggested that on increasing the pH by adding ammonia or ammoniacal buffer solutions, some internal complex compounds are decomposed, giveing rise to soluble ammines.

In the present work we attempt to prove, theoretically, the effect of pH on the yield of reaction product, since an examination only emphasizes the case when the composition of the reaction product remains constant with variation in pH but its amount varies, i. e., the amount of precipitate or color intensity varies. As an example we turn to the interaction of the divalent cation Me·· with the organic substance HR* represented by a weak acid. In this a reaction product of composition MeR_2 is formed, of low solubility, or an intensively colored product representing in the majority of cases, internal complex compounds (weak electroylte):

$$MeR_2 \rightleftarrows Me^{\cdot\cdot} + 2R'. \qquad (1)$$

It follows that,

$$\frac{[Me^{\cdot\cdot}][R']^2}{[MeR_2]} = K_{MeR_2}. \qquad (2)$$

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*Further on, the organic substance HR will be called the reagent.

Taking into consideration the fact that the reagent also represents a weak electrolyte,

$$\frac{[\mathrm{H}^{\cdot}][\mathrm{R}']}{[\mathrm{HR}]} = K_{\mathrm{HR}}, \tag{3}$$

we can rewrite equation (2) in the following form:

$$\frac{[\mathrm{Me}^{\cdot\cdot}][\mathrm{HR}]^2}{[\mathrm{MeR}_2][\mathrm{H}^{\cdot}]^2} = \frac{K_{\mathrm{MeR}_2}}{K_{\mathrm{HR}}^2}, \tag{4}$$

from which

$$[\mathrm{MeR}_2] = \frac{K_{\mathrm{HR}}^2[\mathrm{Me}^{\cdot\cdot}][\mathrm{HR}]^2}{K_{\mathrm{MeR}_2}[\mathrm{H}^{\cdot}]^2}. \tag{5}$$

It follows that the concentration MeR_2, i. e., the yield of reaction product, depends on many factors, in this case on the hydrogen ion concentration. We see also that the yield of reaction product is proportional to the $\mathrm{Me}^{\cdot\cdot}$ concentration which is not known to us. However, $[\mathrm{Me}^{\cdot\cdot}] = C_{\mathrm{Me}^{\cdot\cdot}} - [\mathrm{MeR}_2]$, where $C_{\mathrm{Me}^{\cdot\cdot}}$ is the initial concentration.

We can now speak about the concentration HR. In this case we must take into account the fact that the reagent is usually used in considerable excess and therefore its equilibrium concentration may be said to be practically equal to the initial concentration i. e., $[\mathrm{HR}] \approx C_{\mathrm{HR}}$.

In a case requiring great accuracy, the equilibrium concentration of the reagent may be calculated if we take into consideration the fact that $[\mathrm{HR}] = C_{\mathrm{HR}} - 2[\mathrm{MeR}_2]$.

Taking these remarks into account, we rewrite equation (5) as:

$$[\mathrm{MeR}_2] = \frac{K_{\mathrm{HR}}^2 \cdot C_{\mathrm{HR}}^2 (C_{\mathrm{Me}^{\cdot\cdot}} - [\mathrm{MeR}_2])}{K_{\mathrm{MeR}_2}[\mathrm{H}^{\cdot}]^2}. \tag{6}$$

Resolving this equation with respect to MeR_2 concentration, we find:

$$[\mathrm{MeR}_2] = \frac{K_{\mathrm{HR}}^2 C_{\mathrm{HR}}^2 \cdot C_{\mathrm{Me}^{\cdot\cdot}}}{K_{\mathrm{HR}}^2 C_{\mathrm{HR}}^2 + K_{\mathrm{MeR}_2}[\mathrm{H}^{\cdot}]^2}. \tag{7}$$

In order to find the yield B, of reaction product, we multiply both parts of equation (7) by $100/C_{\mathrm{Me}^{\cdot\cdot}}$:

$$B = \frac{K_{\mathrm{HR}}^2 C_{\mathrm{HR}}^2 \cdot 100}{K_{\mathrm{HR}}^2 C_{\mathrm{HR}}^2 + K_{\mathrm{MeR}_2}[\mathrm{H}^{\cdot}]^2}. \tag{8}$$

The amount of reaction product formed, other conditions being the same, is directly proportional to the initial concentration of the cation [Equation (7)]. However, as Equation (8) shows, the yield of MeR_2 in per cent does not depend on the initial amount of $\mathrm{Me}^{\cdot\cdot}$.

Equation (8) may be expresses in the following form:

$$B = \frac{100}{1 + \dfrac{K_{\mathrm{MeR}_2}[\mathrm{H}^{\cdot}]^2}{K_{\mathrm{HR}}^2 C_{\mathrm{HR}}^2}}. \tag{9}$$

With increasing hydrogen ion concentration, i. e., with increased pH, other conditions being the same, the amount of B is increased. For very low $[H^{\cdot}]$, the second component in the denominator is a small amount and B then reaches prectically 100%. On the other hand, for a large $[H^{\cdot}]$, the second component is a large quantity (100 and more) and there is practically no formation of MeR_2. On increasing C_{HR}, the yield of reaction product goes down. The yield of reaction product depends on the dissociation constants of MeR_2 and HR. Compounds distinguished by high stability, i. e., low dissociation constants, are formed in comparatively larger amounts than compounds with comparatively large constants. Salts of the stronger acids are formed in comparatively smaller amounts. The graphical relationship of the yield of reaction product and pH constructed in accordance with Equation (8) or (9), is shown in Fig. 1. In this way, Equations (8) and (9) reproduce the ascending part of the curve well, i. e. relationship between yield of reaction product and pH. These equations do not enable explanation of thelowering of yield with further increase in pH.

With high pH values, we must discuss the possibility of simultaneous formation of hydroxides $Me(OH)_2$ or complex $Me^{\cdot\cdot}$ compounds with substances entering into the composition of buffered alkaline solutions. Let us consider first the possibility of $Me(OH)_2$ formation, for which

$$\frac{[Me^{\cdot\cdot}][OH']^2}{[Me(OH)_2]} = K_{Me(OH)_2}, \tag{10}$$

where $K_{Me(OH)_2}$ is the product of the first and second dissociation constant of $Me(OH)_2$.

On dividing Equation (10) by (2) we get:

$$\frac{[MeR_2][OH']^2}{[Me(OH)_2][R']^2} = \frac{K_{Me(OH)_2}}{K_{MeR_2}}. \tag{11}$$

At high pH values, we can say that $[R'] \approx C_{HR}$. If we also take into consideration the fact that $[OH'] = \frac{I_{H_2O}}{[H^{\cdot}]}$, then we obtain instead of Equation (11)

$$\frac{[MeR_2]}{[Me(QH)_2]} = \frac{K_{Me(OH)_2} C^2_{HR} [H^{\cdot}]^2}{K_{MeR_2} I^2_{H_2O}}. \tag{12}$$

Equation (12) shows that with decreasing hydrogen ion concentration, i. e., with high pH, the relative amount of MeR_2 decreases. This equation permits the introduction of a correction into the amount of reaction product, calculated according to Equation (9).

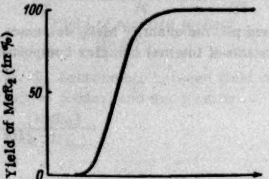

Fig. 1. Dependence of MeR_2 yield on pH.

As examples we calculated the yield of reaction product in relationship to pH, starting approximately according to Equation (9), then we found the relationship $\frac{[MeR_2]}{[Me(OH)_2]}$ for those pH values and so calculated the yield of MeR_2 more exactly (Table 1). In the calculations we put $K_{HR} = 10^{-5}$; $K_{MeR_2} = 10^{-8}$; $K_{Me(OH)_2} = 10^{-15}$; $I_{H_2O} = 10^{-14}$ and $C_{HR} = 10^{-2}$ M.

For very large ratios of $\frac{[MeR_2]}{[Me(OH)_2]}$, $Me(OH)_2$ formation is practically equal to zero and does not affect the quantity MeR_2. When this ratio is comparatively small, then it is not possible to disregard the amount of hydroxide formed. For example, at pH 8, this ratio, in our example is equal to 10 or 10 : 1. Here the yeild of MeR_2 does not amount to 100% as calculated according to Equation (9) and is only $\frac{10 \cdot 100}{10 + 1} = 91\%$ etc.

TABLE 1

Yield of MeR_2 in Relationship to pH

pH	Yield of MeR_2 according to Equation (9) (in %)	$\frac{[MeR_2]}{[Me(OH)_2]}$ according to Equation (12)	Yield of MeR_2 from calculation of $Me(OH)_2$ formation (in %)
1	10^{-2}	10^{15}	10^{-2}
2	1	10^{13}	1
3	50	10^{11}	50
4	100	10^{9}	100
5	100	10^{7}	100
6	100	10^{5}	100
7	100	10^{3}	99.9
8	100	10	91
9	100	10^{-1}	9.1
10	100	10^{-3}	0.1

Thus, for calculating the yield of reaction product with respect to pH, Equations (9) and (12) may be used.

It is understood that these relationships apply not only to MeR_2 but also to reaction products of different composition. For compounds of the general composition MeR_n, we have:

$$B=\frac{100}{1+\frac{K_{MeR_n}[H^{\cdot}]^n}{K_{HR}^n\cdot C_{HR}^n}}, \tag{13}$$

$$\frac{[MeR_n]}{[Me(OH)_n]}=\frac{K_{Me(OH)_n}\cdot C_{HR}^n[H^{\cdot}]^n}{K_{MeR_n}\cdot J_{H_2O}^n}. \tag{14}$$

For cases where decomposition of MeR_n takes place at high pH values, with formation of ammines, instead of Equation (14), we take the analogous equation

$$\frac{[MeR_n]}{[Me(NH_3)_m^{+n}]}=\frac{K_{Me(NH_3)_m^{+n}}\cdot C_{HR}^n}{K_{MeR_n}[NH_3]^m}, \tag{15}$$

which shows that with increasing ammonia concentration, i. e., for increased pH, the quantity MeR_n decreases. Equations (8), (9) and (13) may be used for determining the instability constants of internal complex compounds. Taking Equation (8) or (9) relating to K_{MeR_2}, we get

$$K_{MeR_2}=\frac{K_{HR}^2C_{HR}^2(100-B)}{[H^{\cdot}]^2B} \tag{16}$$

or, in the general form for compounds of composition MeR_n:

$$K_{MeR_n}=\frac{K_{HR}^nC_{HR}^n(100-B)}{[H^{\cdot}]^nB}. \tag{17}$$

Equations (16) and (17) are suitable for investigation of the ascending parts of the curve (Fig. 1) for conditions in which the initial reagent concentration is considerably higher than the initial cation concentration. The instability constant of MeR_n may be calculated knowing the pH; the yield of reaction product B is found experimentally and graphically (Fig. 2), corresponding to the values $\frac{[MeRn]}{[Me(OH)_n]}$, from which K_{MeR_n} is calculated according to Equation (14). It is understood that for this calculation we must be certain that decomposition of MeR_2 takes place at high pH values, with formation of $Me(OH)_2$.

For a known amount of K_{MeR_n}, using this equation, we can calculate $K_{Me(OH)_n}$.

If K_{MeR_n} is known, then the pH value may be found for which the required yield of reaction product is attained. In agreement with Equation (9), we put

$$[H^{\cdot}] = K_{HR}C_{HR}\sqrt{\frac{100-B}{K_{MeR_2}\cdot B}}. \tag{18}$$

then

$$pH = pK_{HR} - \frac{1}{2}pK_{MeR_2} - \quad C_{HR} - \frac{1}{2} \quad \frac{100-B}{B}. \tag{19}$$

Equation (19) shows that the pH required for attaining a given yield of reaction product (in per cent) does not depend on the initial amount of $Me^{\cdot\cdot}$ and may be calculated if K_{HR} and K_{MeR_2} are known, and also the concentration of the reagent taken and the excess of reagent. If we take as the beginning of the reaction the moment when about 1% MeR_2 is formed, (taking the initial amount of $M\bar{e}$ as equal to 100%) and the end of the reaction when 99% MeR_2 is formed, then we are easily presuaded that, with an excess of reagent, this method takes place on varying the pH by 2 units:

$$pH = \left(pK_{HR} - \frac{1}{2}pK_{MeR_2} - \log C_{HR}\right) \pm 1. \tag{20}$$

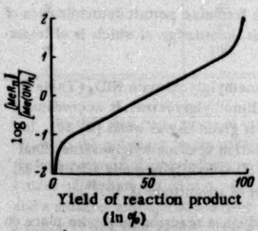

Fig. 2. Relationship between yield of reaction product and the quantity $\frac{[MeR_n]}{[Me(OH)_n]}$,

The pH values within the limits of the two units may be called the field of formation of the reaction product (for sparingly soluble compounds – the field of precipitation).

Deriving these calculations, we find that the field of formation of MeR embraces four pH units, and 1.33 for MeR_3.

Equations (12) and (14) permit calculation of the pH at which decomposition of MeR_n starts and finishes with formation of $Me(OH)_n$. For example, let us look at Equation (12). We will take as the beginning of decomposition of MeR_2, the moment when 1% $Me(OH)_2$ is formed from it. Then, instead of (12), we can write

$$\frac{100}{1} = \frac{K_{Me(OH)_2}C_{HR}^{2}[H^{\cdot}]^{2}}{K_{MeR_2}I_{H_2O}^{2}}, \text{ so that } [H^{\cdot}] = \frac{10\,I_{H_2O}}{C_{HR}}\sqrt{\frac{K_{MeR_2}}{K_{Me(OH)_2}}},$$

and it follows

$$pH = pI_{H_2O} + \log C_{HR} - \frac{1}{2}\log\frac{K_{MeR_2}}{K_{Me(OH)_2}} - 1. \tag{21}$$

For practically complete decomposition of MeR_2, to the corresponding hydroxides, we have:

$$\frac{1}{100} = \frac{K_{Me(OH)_2} C_{HR}^2 [H^{\cdot}]^2}{K_{MeR_2} \cdot l_{H_2O}^2}, \text{ so that } [H^{\cdot}] = \frac{l_{H_2O}}{10C_{HR}} \sqrt{\frac{K_{MeR_2}}{K_{Me(OH)_2}}},$$

which signifies

$$pH = pl_{H_2O} + \log C_{HR} - \frac{1}{2} \log \frac{K_{MeR_2}}{K_{Me(OH)_2}} + 1. \tag{22}$$

In this way the field of decomposition of MeR_2 embraces 2 pH units. Within the limits of pH significance (from the end of MeR_2 formation to the beginning of its decomposition), there is a practically complete yield (100%) of reaction product. The extent of this field may be found by subtracting the pH at the end of MeR_2 formation [Equation (20)], from the pH at the beginning of decomposition [Equation (21)].

$$pH_{begin} - pH_{end} = 12 + pK_{MeR_2} - pK_{HR} - \frac{1}{2} pK_{Me(OH)_2} + 2 \log C_{HR}. \tag{23}$$

Thus, the field of complete procedure of the reaction is shown to be wider than the high pK_{MeR_2} and the low pK_{HR} and $pK_{Me(OH)_2}$. From the subtracted amounts in Equation (23), only the concentration of the reagent may be varied experimentally when it is larger than the widest field for complete reaction procedure. Higher concentrations of the reagent, by 10 times, brings about an extension of this field by 2 pH units.

It is probable that when decomposition of MeR_2 with formation of $Me(OH)_2$ begins earlier, then complete formation of MeR_2 is attained, i. e., when $pH_{begin.} < pH_{end}$. As may be seen from Equation (23), this is possible under conditions such that

$$12 + pK_{MeR_2} + 2 \log C_{HR} < pK_{HR} + \frac{1}{2} pK_{Me(OH)_2}.$$

Under these conditions, complete formation of MeR_2 cannot be attained for one single pH value.

All the preceding formulae describe well the qualitative side of the question under consideration, however, the calculations may result not only in experimental errors, but also in approximate figures for some of the amounts (for example, C_{HR}) and other moments. Nevertheless the preceding formulae permit determination of the order of magnitude of instability constants of internal complex compounds, knowledge of which is of importance from the theoretical and practical points of view.

Using Equation (16) we calculated the instability constant of nickel dimethylglyoximate NiD_2 (Table 2). For this we take into consideration the fact that the dissociation constant of dimethylglyoxime, in accordance with [27], is equal to $8 \cdot 10^{-12}$. The dependence of NiD_2 precipitation on pH is given in the works [2, 10]. In these investigations, 9.8 mg $Ni^{\cdot\cdot}$ was precipitated by 15 ml 1% alcoholic solution of dimethylglyoxime, final volume 100 ml; from this the nickel concentration is equal to $1.67 \cdot 10^{-3}$ M, dimethylglyoxime is $1.3 \cdot 10^{-2}$ M. In this way the instability constant of nickel dimethylglyoximate has an order of magnitude of 10^{-18}.

It should also be kept in mind that, in accordance with the method studied, a reaction may take place on which attention has often not been focussed, the course of which affects the amount of compound formed. We have in mind a complex formation reaction between cations of interest to us and salts entering into the composition of buffered solutions (particularly with phosphates, citrates, etc.). It is known that many different mixtures form solutions of definite pH value. We investigated the relationship between the composition of a buffered solution and the amount of reaction product formed. This relationship is particularly easy to study on examples of extracted compounds, such as the amount of extracted reaction product located in the first link, with the amount of the compound being formed. For the investigation, acetate, diphthalate, citrate and citrate-phosphate buffered mixtures, with the same pH values, were used. Buffered solutions were prepared according to data in the literature [28, 29]; the pH was measured by the electrometric method. Investigations were carried out with zinc dithizonate.*

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*Z. Moseev participated in this part of the work.

TABLE 2

Precipitation of Nickel Dimethylglyoximate at Different pH and Calculation of its Instability Constant

pH	Nickel precipitated (in %)	Equilibrium concentration of dimethylglyoxime ($M \cdot 10^2$)	$K_{NiD_2} \cdot 10^{18}$
3.0	5	1.29	0.2
3.5	30	1.2	0.21
4.0	70	1.07	0.31
4.2	75.5	1.06	0.56
4.2	84.7	1.02	0.27
5.0	93.5	1.00	4.4
5.0	98.0	0.97	1.2

Two ml of a solution of the zinc salt and 1 ml buffered solution were shaken up for 15-30 minutes with 1 ml 0.1% dithizone solution in chloroform. The amount of zinc dithizonate extracted was determined radiometrically with the aid of the radioactive zinc isotope Zn^{65} (Table 3, Fig. 3).

TABLE 3

Extraction of Zinc Dithizonate in Relationship to pH and Composition of Buffer Mixture (50 γ Zinc in 3 ml Buffered Solution)

pH	Buffered mixture			
	acetate	diphthalate	citrate	citrate-phosphate
	extraction of zinc (in %)			
3	45	62	51	45
4	97	93	63	62
5	100	100	72	71
6	–	100	92	85

In this way two groups of buffered solutions may be distinguished: 1) buffered solutions, the components of which do not react in practice with the cations studied (acetate, diphthalate solutions); 2) buffered solutions the components of which form compounds of low dissociation, complex, or sparingly soluble compounds (citrate, citrate-phosphate solutions), with the cations studied. When using buffered solutions, the second group is formed and a smaller amount of reaction product is extracted than for exactly the same pH value formed by a buffered solution of the first group. The process according to this method may be represented by the equation

$$MeR_n + mAn^{3-} + nH^{\cdot} \rightleftarrows [MeAn_m]^{3m-n} + nHR, \qquad (24)$$

where An^{3-} is the anion salt entering into the compositionof the buffered solution (for example, PO_4^{III}). With increasing hydrogen ion concentration, the equilibrium is displaced to the left, i. e., to the side of formation of a large amount of internal complex compound of interest to us. This relationship is seen in the data given in Table 3 and in Fig. 3.

As Equation (24) shows, an increased reagent concentration must displace the equilibrium to the left and remove $[MeAn_m]^{3m-n}$ formation to a conconsiderable extent. This relationship is illustrated in Fig. 4 and 5 (here 10γ $Zn^{\cdot\cdot}$ of $Cd^{\cdot\cdot}$ was contained in 2 ml solution to which was added 1 ml buffered solution).* In one case, extraction produced 1 ml 0.01% dithizone solution, in a second – 0.1% solution. We see that increasing concentration of reagent led to a sudden increase in the amount of reaction product extracted and removal of the effect of the composition of the buffered solution. It should be mentioned that 1 ml solution contained a sufficient amount of dithizone to combine with the amount of zinc taken. If the instability constant MeR_n is considerably lower than the corresponding amount $[MeAn_m]^{3m-n}$, then MeR_n is formed predominatly and the composition of the buffered solution either does not affect the amount of reaction product formed at all, or else affects it very little. This was observed by us on extraction of mercury dithizonate.

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*The amount of zinc or cadmium extracted was determined radiometrically.

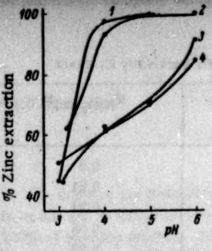

Fig. 3. Effect of composition of buffered mixtures on zinc dithizonate extraction. 1) acetate, 2) diphthalate, 3) citrate 4) citrate-phosphate.

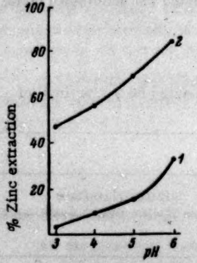

Fig. 4. Extraction of zinc dithizonate (10γ Zn·· in 3 ml phosphate-citrate buffer solution). 1) 1 ml 0.01% dithizonate solution in $CHCl_3$, 2) 1 ml 0.1% dithizonate solution in $CHCl_3$.

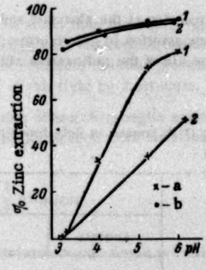

Fig. 5. Extraction of cadmium dithizonate (10γ Cd·· in 3 ml buffer solution). Buffered solutions: 1) diphthalate, 2) citrate-phosphate (a – 0.01% dithizonate solution b – 0.1% dithizonate solution).

SUMMARY

1. The dependence of yield of reaction product between cation and organic substance on a series of factors has been shown and particularly on the pH of the solution.

2. Data are given relating to the field of formation, field of decomposition of the reaction product and the field of complete procedure of the reaction and equations derived for their calculation.

3. It has been shown that the amount of reaction product formed and extracted, is affected by the composition of the buffered solution used for establishing a given pH value.

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Gorky State University

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POLAROGRAPHIC STUDY OF THE KINETICS OF POLYMERIZATION PROCESSES

M. I. Bobrova and A. N. Natveeva

Up to recent times the dilatometric method has been used widely for the study of kinetics of polymerization, as visualized in this series of studies [1, 2]. In other work [3], the weight of polymer has been determined as a function of the time.

The dilatometric method is not always satisfactory with reference to requirements of accuracy, particularly in the case of total completion of the polymerization process and also in the case of copolymerization.

In a study of complete polymerization, by Bevington, Melville and Taylor, [4], the method of labelled atoms was used.

The use of the polarographic method for a study of kinetics of polymerization and particularly for a study of kinetics of copolymerization, appears to be very promising, owing to the accuracy and speed of the determination of deep-seated polymerization and copolymerization and also of the composition of the polymer. In spite of the fact that many monomers, particularly methyl methacrylate, may be determined polarographically [5] a study of polymerization kinetics by this method, when applied to combined and solid samples, has met with considerable difficulty, in connection with the recovery of the residual monomer. We worked out a polarographic method for the study of polymerization kinetics, using methyl methacrylate as an example, in presence of 2, 2'-azobisisobutyronitrile in the role of activator. The main object of this was the complete recovery of the monomer from the solidified sample and offered the possibility of widespread use of polarography for the study of different polymerization and copolymerization processes.

EXPERIMENTAL

Polymerization and recovery of monomer from a solidified sample of polymer. Polarography was carried out in the Gorkovsky polarograph, model M-7, fitted with a mirror galvanometer, the sensitivity of which was equivalent to 150 MM/μa . The measurements were carried out on the basis of shunt 1/10.

Aqueous alcoholic solutions of $(C_4H_9)_4NI$ and LiCl were used as supporting electrolytes.

Cylindrical capillary, t = 3 sec., $m^{2/3} \cdot t^{1/6} = 1.83$ mg$^{2/3}$ sec$^{-1/2}$ for a voltage of 2.1 V.

The height of the rising mercury bulb offered the possibility of decreasing the tangential motion [6].

Polymerization was carried out in cylindrical ampoules made of capillary glass, 5-7 mm diameter, height 60-70 mm. Into the ampoules was introduced by means of a pipette, a mixture (1 g) of a definite amount of methyl methacrylate and 0.1% 2, 2'-azobisisobutyronitrile. The ampoules were sealed and suspended on hooks in a tall water bath. The ampoules were removed from the bath at definite intervals of time and placed in a small porcelain dish with a definite amount of ethyl alcohol (5-10 ml). Then the glass rod of the ampoule was crushed and the monomer in the sample dissolved, if the sample was still liquid; in the case where it was slightly viscous, it had to be pulverized with a glass rod.

For recovery of unpolymerized monomer from a solidified sample of polymer, we proposed the construction of an apparatus, consisting of the following basic details: a steel cylinder (height 45 mm, internal diameter 26 mm, thickness of wall, 6 mm) in which was placed at one side at an angle of 85°, a funnel 55 mm long, 6 mm diameter, with an internal rod driven by a worm in a coupling fitted with a screw on this funnel. On the front part of the glass cylinder, two shafts were arranged to right and left, by means of which the cylinder was made fast to the cover by two hooks. In the central opening of the cover there was a boss with the aid of which it was fastened on to the shaft of the motor of an end mill. The cover was joined to the body of the apparatus as a whole.

The distance of the teeth of the mill from the edge of the funnel was reduced to a minimum. The sample was added via the funnel, to the cylinder filled with a solvent for the monomer, in the present case, 5 ml ethyl alcohol, the motor was switched on, the mill rotated and gradually the propellor moved the sample in the direction of the mill.

In this way the rod of polymer in a medium consisting of a solvent for the monomer, was converted practically without residue, into very fine shavings. The solution obtained was filtered through glass wool. An amount of solution corresponding to 0.05 ml was removed by means of a micropipette and introduced into an electrolyzer containing a mixture of supporting electrolyte and solvent (2.5 ml LiCl + 2.5 ml ethyl alcohol); then the amount of monomer determined polarographically and the extent of polymerization for a given moment of time, was obtained.

For determination of the complete extraction of the monomer, in the present method of extraction of monomer from the sample, another similar sample of polymer was converted to very fine shavings in exactly the same way, however monomer and polymer were already present together in the solvent medium.

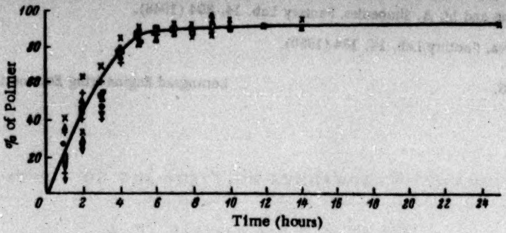
In the case of polymethyl methacrylate, with reference to the solvent, we took 10 ml of a mixture of equal volumes of benzene and methyl alcohol. Finally, from the simultaneously ground and dissolved polymethyl methacrylate, there is obtained a homogeneous liquid solution of the polymer and monomer together. Final addition of 10 ml ethyl alcohol to the solution formed, resulted in precipitation of the polymer on carefully mixing the contents of the cylinder. A test for complete precipitation was made immediately the precipitant was selected. A sample of 0.05-0.1 ml was then removed by micropipette and placed in an electrolyzer containing a mixture of 3 ml supporting electrolyte solution $(C_4H_9)_4NI$ (C = 0.1 M), 6 ml ethyl alcohol and 1 ml of a mixture of equal volumes of benzene and methyl alcohol. Polarography gave the amount of monomer left in the given sample of polymethyl methacrylate. For calculating the value of the diffusion current constant of methyl methacrylate determined by us in the preceding mixture, at the same time as in the first case, the value found for the diffusion current constant of mixtures of 2.5 ml LiCl + 2.5 ml ethyl alcohol, was used. As shown, with repeated solution and precipitation of this same sample, with subsequent polarography, there may be a certain amount of monomer entrapped in the precipitate polymer mass. Therefore, checking for completeness of extraction of the polymer was followed by carrying out a two-fold repetition of the cycle in the order: initial grinding with simultaneous solution of the polymer in a mixture of benzene and methyl alcohol, removal of samples for polarography, decanting of the solution, careful superficial washing of the mass of polymer with ethyl alcohol, decantation, second dissolution of the polymer in a mixture of benzene and methyl alcohol, precipitation of the polymer with ethyl alcohol, removal of the sample for polarography, etc., if necessary introduction of corresponding recovery.

The amount of monomer in the solution of polymer may be determined in the following way: after formation of the polymethyl methacrylate solution in a suitable quantity of a mixture of benzene and methyl alcohol, a sample was removed, equivalent to 0.05 ml and placed in the electrolyzer which contained a mixture of supporting electrolyte and a solvent of composition indicated above. The polymer formed on this film was removed by means of a glass rod and the solutions polarographed.

On account of the complexity with which the chain reaction proceeds, a comparison was made of the average values for the amount of residual monomer on extracting it with alcohol from the shavings formed and the amount of monomer determined from the large number of similar samples in the total polymethyl methacrylate solution, precipitation of this, etc., permitted the attaining of a result relating to the suitable sample offered for extraction of residual monomer from the required sample of solidified polymer (Table).

The kinetics of the process of polymerization of methyl methacrylate in presence of 0.1% 2, 2'-azobisisobutyronitrile, at 60°, determined polarographically, are illustrated in the form of a curve, in the figure.

The amounts of unpolymerized monomer based on many experiments, for the first 3 hours, differ widely from each other. In the solidified sample, this difference disappears and this may be explained by the greater free development of the chain reaction in the initial stages of the polymerization process.



Curve of kinetics of process of polymerization of methyl methacrylate with 0.1% 2, 2'-azobisisobutyronitrile.

TABLE

Kinetics of Deep-Seated Polymerization of Methyl Methacrylate at 60° with 0.1% 2, 2'-Azobisisobutyronitrile

Polymerization time (in hours)	Polymer content (in %) (average figure)		Polymerization time (hours)	Polymer content (in %) (average figure)	
	monomer extraction with ethyl alcohol	solution of polymer in a mixture of benzene and methyl alcohol (1:1)		monomer extraction with ethyl alcohol	solution of polymer in a mixture of benzene and methyl alcohol (1:1)
1	20	21	8	92	88
2	42	39	9	92	90
3	51	47	10	93	91
4*	78	80	12	92	92
5	86	86	14	96	93
6	89	90	25	93	93
7	91	90			

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*Beginning with 4-hourly samples extraction of the monomer was carried out by the method described above.

SUMMARY

1. Details of construction of an apparatus have been proposed for extraction of unpolymerized monomer from solidified samples of polymer.

2. The value of the diffusion current constant has been determined for methyl methacrylate in the mixtures: ethyl alcohol – benzene– methyl alcohol.

3. The kinetics of deep-seated polymerization of methyl methacrylate in presence of 0.1% 2, 2'-azobisisobutyronitrile, have been determined at 60°.

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STUDY OF THE SORPTION EXCHANGE OF ORGANIC IONS

A. T. Davydov and R. F. Skoblionok

In the practical usage of contemporary ionites, the separation of organic and inorganic ions from their mixtures is of great importance. There is a need for a qualitative study of the mechanism of adsorption exchange of organic ions which is dictated by the development of new fields such as the separation of substances by adsorption techology [1], on which is based the method of continuous flow in a primary chromatographic column.

In the present investigation we put forward the problem – a study of the behavior of organic ions on exchange with inorganic ions and the elucidation of the influence of the nature and size of the ion on the extent of sorption exchange.

For carrying out the investigation we took salts of bases of the aliphatic and aromatic series – methylamine and aniline hydrochlorides, as they are easily soluble and dissociate well in aqueous solutions.

With the object of confirming the possible use, found earlier, of the mechanism of exchange of inorganic ions for adsorption exchange of organic ions, we linked the required checking of the application of the Gapon equation of isothermal adsorption exchange [2], with our case.

The investigations were carried out on the thiocarbonate, saturated with calcium ions. We studied the exchange of Ca^{2+} on $CH_3NH_3^+$ and $C_6H_5NH_3^+$ from solutions of their hydrochlorides of different concentrations. Five grams weighed portions of Ca thiocarbonate were placed in special flasks, 50 ml of the solution under test, in a suitable concentration, was poured over and the mixture left to stand for 48 hours with frequent shaking. After 48 hours the flasks and their contents were placed in a thermostat (25°), after which samples were removed for analysis. The amount of calcium desorbed was determined in equilibrium solutions by the exchange method. In the case of exchange of Ca^{2+} for $C_6H_5NH_3^+$, the equilibrium concentrations of the latter were determined; the determinations were carried out potentiometrically by titrating with sodium nitrite in a hydrochloric acid medium [3].

For the case of exchange under investigation, the Gapon equation has the following form:

$$\frac{1}{a} = \frac{1}{a_m} + \frac{K}{a_m} \frac{\sqrt{\frac{a}{2}}}{100C_0 - a},$$

where $\underline{a}$ is the amount in milligram-equivalents of the organic ion adsorbed by 10 g adsorbent and is equal to the amount in milligram-equivalents of Ca^{2+} desorbed; a_m is the maximal adsorption, calculated for 10 g adsorbent; C_0 is the initial concentration of the substituent ion (in milligram-equivalents/ml); K is the exchange constant.

Experimental and calculated data are given in Tables 1 and 2.

The values $\underline{y}$, a_m and K were calculated by the method of least squares.

On comparing the amount of desorbed Ca^{2+} with the amount of adsorbed $C_6H_5NH_3^+$, in fields of high concentration, we observed a difference which cannot be due to experimental error. Evidently here there is apolar adsorption of aniline hydrochloride, which is shown to a greater extent with increasing concentration of

TABLE 1

Calculation of Gapon Equation Isotherms for the System: Ca Thiocarbonate + CH_3NH_3Cl

Initial concentration (C_0) CH_3NH_3Cl (in N)	Amount of Ca^{2+} (a) desorption from 10 g adsorbent (in mg-equivalents)	$x = \frac{\sqrt{\frac{a}{2}}}{100C_0 - a}$	$y = \frac{1}{a}$
0.05	2.19	0.3724	0.458
0.10	3.40	0.1975	0.292
0.25	5.40	0.0838	0.185
0.50	6.96	0.0433	0.146
0.75	7.58	0.0289	0.132
1.000	7.98	0.0217	0.126

Note: $a_m = 9.6 \pm 0.1$, $K = 9.1 \pm 0.2$, $\sigma_y = 0.001$. (σ_y is the average square deviation for individual determinations of y).

the solution. Studying the possibility of apolar adsorption for calculating the exchange isotherms $[Ca^{++}] + C_6H_5NH_3^+$, we started from the relationship found for equilibrium concentrations:

$$\frac{1}{a} = \frac{1}{a_m} + \frac{K}{a_m} \frac{\sqrt{\frac{a}{2}}}{100C}.$$

It is seen from the preceding data that the Gapon equation is completely applicable to exchange between inorganic and organic ions. This is confirmed by the low values for average square deviations of individual determinations and the low average square deviations for the average values of the isothermal constants (a_m, K).

TABLE 2

Calculation of Gapon Equation Isotherms for the System Ca Thiocarbonate + $C_6H_5NH_3Cl$

Initial concentration (C_0) of $C_6H_5NH_3Cl$ (in N)	Equilibrium concentration (C) of $C_6H_5NH_3Cl$ (in N)	Amount of $C_6H_5NH_3^+$ (C') adsorbed by 10 g adsorbent (in mg-equivs.)	Amount of Ca^{2+} (a), desorbed from 10 g adsorbent (in mg-equivs.)	$x = \frac{\sqrt{\frac{a}{2}}}{100\ C}$	$y = \frac{1}{a}$
0.05	0.005	4.5	4.80	3.1750	0.211
0.10	0.012	8.8	8.48	1.7159	0.121
0.25	0.110	14.0	12.65	0.2286	0.078
0.50	0.336	16.4	14.02	0.0788	0.072
0.75	0.564	18.6	14.46	0.0477	0.070
1.00	0.797	20.3	14.88	0.0342	0.069

Note: $a_m = 15.3 \pm 0.9$, $K = 0.64 \pm 0.17$, $\sigma_y = 0.009$.

The considerably higher adsorption of the aniline ion compared with the methylamine ion is explained by its larger ionic radius; the radius of the ion $C_6H_5NH_3^+$ (~ 7A), for example, is twice as large as the radius $CH_3NH_3^+$ (~3A).

SUMMARY

1. A study has been carried out of exchange sorption of organic cations of the aliphatic and aromatic series (methylamine and aniline) on Ca thiocarbonate.

2. Application of the Gapon equation to the adsorption exchange reaction between calcium and organic ions is confirmed by the satisfactory state of the constants obtained.

3. On sorption exchange between calcium ions and aniline, the exchange equivalence is displaced into fields of high concentration; this is probably explained by the better apolar sorption.

4. The figure for the sorption exchange is markedly increased with increased size of organic ions.

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Kharkhov State University

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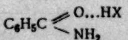
COMPLEX FORMATION OF ACETAMIDE AND BENZAMIDE WITH OTHER ORGANIC COMPOUNDS

N. D. Strelnikova

In the literature connected with complex-formation reactions of amides, there is rather a lot of data on the characteristics of the reactivity of acetamide and benzamide. In the case of acetamide, the complex compounds most completely represented are with inorganic substances – salt-formation products combined with acids of the type $CH_3CONH_2 \cdot HNO_3$ [1] or $2CH_3CONH_2 \cdot HBr$. The great amount of complex formation of salts of metals of practically all groups of the periodic system is well known where molecules of acetamide fulfill the function of adducts [2-6]. The existence of the compound $CH_3CONH_2 \cdot Br_2$ [7] has been shown conductometrically. All the substances enumerated are formed as the result of combining acetamide with reagents of the electron-donor type.

Organic complexes of acetamide are known, mainly with substances possesing electron-acceptor functions. Salt-formation products of acetamide with tartaric and salicylic acids [5] have been isolated, and were detected by the method of thermal analysis of compounds with acetic, valeric and lauric acids having a 1:1 composition [8]. The many compounds of acetamide with reagents possessing a mixed type of reactivity are well known. The most completely established here is the group of phenolic products. Acetamide forms compounds with a 1:1 composition with pyrocatechol, hydroquinone, β-naphthol, and with phenol, $CH_3CONH_2 \cdot 2C_6H_5OH$ [5]. Of complexes with substances containing a nitro group, compounds of acetamide with m- and p-nitrophenols and picric acid, are known [9]. We did not succeed in detecting complex-formation of acetamide with water, by the fusion method [8]. A typical donor – nitrosodimethylaniline, forms compounds with acetamide which have been isolated by Kremann [10]. Eutectics have been obtained by the method of thermal analysis of binary systems of acetamide with other organic compounds – hydrocarbons, alcohols, ketones [11, 12].

Complex-formation of benzamide has been studied to a slight extent. In this connection, cases of formation of complex compounds with halogan hydrides of probable structure  $C_6H_5C\begin{smallmatrix} \nearrow O...HX \\ \searrow NH_2 \end{smallmatrix}$ [5], with metallic halides and with a very small number of organic acids, are also known; for example, products have been isolated by linking high melting point acids with m- and p-hydroxybenzoins [5]. Compounds have been detected with benzoic acid [12]. Complex-formation products of benzamide with phenol, of composition 1:1, are known, with hydroquinone (2:1), m- and p-nitrophenols (1:1) [5].

It is concluded from these data that acetamide and benzamide possess electron-donor reactivity. Great interest is attached to a study of complex-formation of acetamide and benzamide with substances displaying only an electron-donor function.

In order to decide the question of the type of reactivity possessed by acetamide and benzamide, investigations were carried out on forty binary systems. In twenty systems, acetamide complex-formation was studied and in twenty – benzamide. Organic substances with acknowledged electron-donor function (p-toluidine, benzidine, naphthylamine, diphenylamine) definite acceptors (benzoic, adipic, stearic acids), compounds with a mixed type of reactivity – amides (carbamide, thiocarbamide), phenols (phenol, pyrocatechol, resorcinol, hydroquinone, α- and β-naphthols) and nitro compounds (p-nitrotoluene, α-nitronaphthalene) were studied as the second component of the system.

Acetamide, twice-distilled, dried and stored over P_2O_5, was used for the work. It melted at 82°. Benzamide was purified by repeated recrystallization from a hot solution, the pure preparation melted at 128°. Purification of the remaining substances, tests for authenticity and purity, were carried out by the usual methods. The purity or the phenols was again controlled by the method of B. V. Tronov and L. P. Kulev [12-15], disclosure of contamination by the usual methods not being suitable. After purification, all the compounds had compositions and constants close to those indicated in the literature. The investigations were carried out by the thermal analysis method. The method of carrying out the tests was the usual one [12-16].

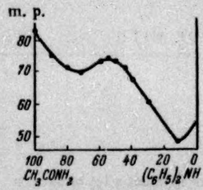


Fig. 1. Fusibility of the system acetamide – diphenylamine.

In the majority of the systems with acetamide, eutectics of varying composition were discovered, with a variety of melting points (acetanilide, phenacetin, p-toluidine, α- and β- naphthylamines, benzamide, carbamide, organic acids). A definite maximum was disclosed on the fusion diagram for acetamide–diphenylamine, indicating the formation of a chemical compound (1:1) (Fig. 1). In systems consisting of p-nitrotoluene and α-nitronaphthalene, melts of the components were not miscible among themselves.

With phenols – carbolic acid, resorcinol, pyrocatechol – on studying the fusibility, only extreme points in the diagram were obtained (Fig. 2, a and 2, b); within the limits 40-70 mol.% acetamide there is an area of transparent, viscous, vitreous solutions which solidify on cooling. Crystallization does not set in these systems even after 6 months storage. In the binary system with hydroquinone, a maximum was detected for a ratio of the components of 1:1.

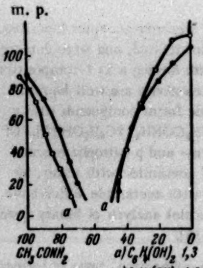


Fig. 2. Fusibility of the system acetamide – resorcinol (a) and acetamide – pyrocatechol (b).

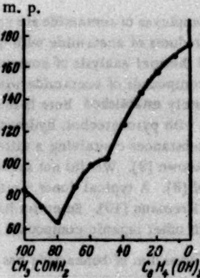


Fig. 3. Fusibility in the system acetamide – hydroquinone.

In the case of benzamide, eutectics were obtained with acetamide and carbamide for various crystallization temperatures. In the fusibility diagram for benzamide – thiocarbamide (Fig. 4) the compound

$$C_6H_5CONH_2 \cdot 2(NH_2)_2CS$$

was detected and melted at 138.4° with two eutectics. Normal curves with one simple eutectic were given by benzamide, acetamide, phenacetin, p-toluidine, benzidine, maphthylamines. The result with phenols varied – with carbolic acid there was a eutectic at 80 mol. % of the phenol, resorcinol (Fig. 5), gave a chemical compound melting at 86.8° and two eutectics. In the case of pyrocatechol we only succeeded in constructing the lateral branch of the fusibility diagram, since in the area 40-60 mol. % benzamide, non-crystallizing viscous, vitreous solutions were obtained, which solidified on powerful cooling. Hydroquinone, α- and β-naphthols, gave deep eutectics with benzamide in the area 50 mol.% benzamide. A similar result was obtained in benzamide systems with nitro compounds and organic acids.

The capacity of amides to form salts with acids, complex and intracomplex compounds [4] with salts of metals, indicates the better electron-donor properties of acetamide and benzamide these being expressed more strongly for acetamide than for benzamide. Complex compounds of acetamide are more numerous, more varied in composition and more stable. Many of them have been isolated in the free state. In the literature [9], complex formation of acetamide and benzamide with phenols, has been mentioned and has been confirmed by our investigations. On interaction with phenols, acetamide, as is to be expected, was shown to be more reactive than benzamide. In the system acetamide–hydroquinone, the incongruently melting compound $CH_3CONH_2 \cdot C_6H_4(OH)_2$ (Fig. 3), is noted on the fusibility curve. In systems with resorcinol and pyrocatechol, in the area for compound formation detected by Kremann and Wenzig, we obtained vitreous solutions, which solidified much earlier than the compounds detected [17], of composition 1:1; in the case of phenol and acetamide, the area of these viscous, vitreous solutions corresponds to a composition of the complex compound, of 2:1, also detected earlier by Kremann. For benzamide, we obtained complex compounds with resorcinol (1:1) (Fig. 5) similar to the date of Kremann [9] with pyrocatechol, also in the form of vitreous solutions. In the case of phenol, hydroquinone, α- and β-naphthols, eutectics were obtained which did not permit of any conclusions as to the presence in the systems of chemical interaction. However, all the facts relating to compounds of acetamide and benzamide with phenols do not give a definite basis for judging the type of reactivity of amides, since phenols display complex-formation of a mixed type [4]. Only one chemical compound has been indicated in the literature, of acetamide with an electron-donor reagent – nitrosodimethylaniline [10]. We have mentioned the second case of such a reaction: formation of complex compounds with diphenylamine. Thus, acetamide undoubtedly possesses a double type of reactivity.

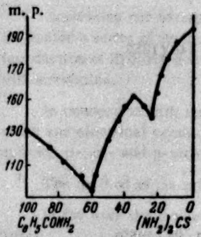


Fig. 4. Fusibility in the system benzamide–thiocarbamide.

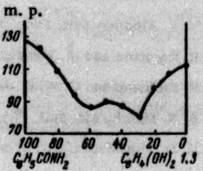


Fig. 5. Fusibility in the system benzamide–resorcinol.

In the case of benzamide, complex compounds have not been detected with thiocarbamide and resorcinol. With the other compounds – naphthylamines, benzidine, p-toluidine, acetanilide, phenacetin, only eutectics have been found; on the basis of the thermal data studied, it follows that conclusions can only be made about the electron-donor properties of benzamide.

SUMMARY

1. There have been studied by the thermal method of analysis, 40 binary systems, composed of the simplest amide representatives, acetamide and benzamide and organic compounds with a definite type of reactivity: amides, phenols, nitro compounds, carboxylic acids.

2. In eight systems, chemical interaction was detected.

3. From a comparison of the data obtained it is seen that acetamide has a mixed type of reactivity, with a predominant electron-donor function.

4. Benzamide has an electron-donor type of activity.

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Tomsk Polytechnic Institute

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STUDY OF INTERACTION OF ACETAMIDE WITH PHENOLS BY PHYSICOCHEMICAL METHODS OF ANALYSIS

Z. K. Dzhelomanova, N. Z. Rudenko and D. E. Dionisyev

Continuing our investigations in the field of interaction of acetamide with acids [1] in the present work we studied a series of systems formed by acetamide and some phenols, with the object of finding out how the introduction of hydroxy and nitro groups into the phenol molecule affects the character of chemical interaction with acetamide.

In connection with the above we studied by physicochemical methods of analysis (fusibility, density, viscosity and electrical conductivity), binary systems of acetamide with phenol, pyrocatechol, resorcinol, hydroquinone, o-, m- and p-nitrophenol, 2, 4-dinitrophenol and 2, 4, 6-trinitrophenol.

The method of investigation was as formerly [2].

In the work the concentrations are everywhere expressed in molecular percentages, the viscosity in centipoises.

EXPERIMENTAL

Purification of the basic component – acetamide, was carried out exactly as before [1]; m. p. 79.4°, d_4^{80} 0.9990 and η^{80} 1.61.

The system acetamide – phenol was studied by the Kremann and Wenzing fusion [3]. They established the formation of the compound $CH_3CONH_2 \cdot 2C_6H_5OH$. We repeated the fusion study and also the investigation of density, viscosity, electrical conductivity at 65, 75 and 85°. Phenol was purified by the method described earlier [2] and had a m. p. 41°. On investigating the fusibility, we obtained several different results. The fusibility curve consists of three crystallization branches: two – of the pure components, and one – the compound $CH_3CONH_2 \cdot 2C_6H_5OH$. Eutectic points of composition 55 and 10 mol. % acetamide, m. p. of 29 and 30.2°

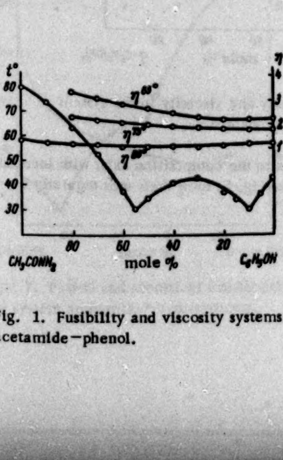

Fig. 1. Fusibility and viscosity systems of acetamide – phenol.

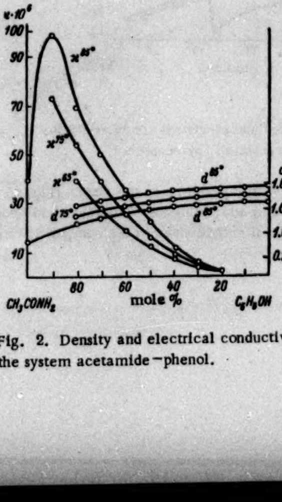

Fig. 2. Density and electrical conductivity of the system acetamide – phenol.

(according to Kremann: 46 and 8 mol. % acetamide, m.p. of. 27 and 27.5°)(Fig. 1). Melting point of compoun 42.5° (according to Kremann: 40.8°). Viscosity isotherms were slightly convex to the composition axis (Fig. 1). The density curves were convex from the composition axis (Fig. 2). Electrical conductivity increases with increase in acetamide concentration and at a temperature of 85° passes through a maximum in the region of 90 mol% acetamide and then falls. The value of the electrical conductivity at the maximum point is 2.5 times as large as the electrical conductivity of acetamide (Fig. 2).

System acetamide–pyrocatechol. An attempt at a study of this sytem was made by Kremann and Auer [4], with reference to fusibility, a total of 3 melting points being obtained.

We studied the present system with reference to viscosity, density and electrical conductivity at 80, 95 and 110° and also for fusibility.

For the work we purified pyrocatechol, resorcinol and hydroquinone as before [5]. Pyrocatechol had a m. p. 105°.

The fusibility curve consists of three parts: two of the pure components, and one – an incongruently melting compound (Fig. 3). A eutectic point at 46 mol. % acetamide and 26°, transition point at 74 mol. % acetamide and 37.6°. The viscosity curves (Fig. 3) were convex from the composition axis, just as in the case of the density curves (Fig. 4). Electrical conductivity isotherms (Fig. 3) have a definite maximum in the region of 80 mol. % acetamide.

System acetamide–resorcinol was studied earlier for fusibility, very superficially (2 points) [4].

We studied fusibility, also viscosity, density and electrical conductivity in the system at 95, 105 and 115°. Resorcinol had a m. p. 110°.

It was not possible to obtain a complete fusibility curve since in the region from 70 to 40 mol. % acetamide, mixtures are not capable of crystallization. The use of primers, vigorous mixing and intense cooling did not give positive results. On cooling to –20° the solid vitreous mass became brittle.

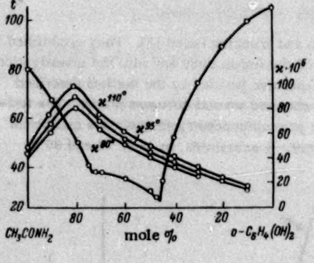

Fig. 3. Fusion and electrical conductivity in the system acetamide–pyrocatechol.

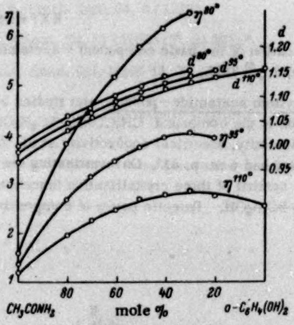

Fig. 4. Density and viscosity in the system acetamide–pyrocatechol.

The viscosity isotherms in the system (Fig. 6) are slightly convex to the composition axis; with increasing temperature they straighten out. The electrical conductivity isotherms (Fig. 5) show their own regularly descending curves slightly convex to the composition axis.

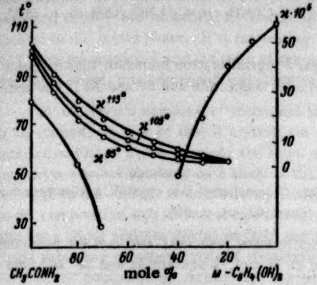

Fig. 5. Fusion and electrical conductivity in the system acetamide—resorcinol.

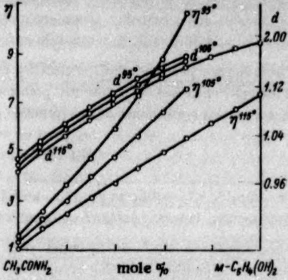

Fig. 6. Density and viscosity in the system acetamide—resorcinol.

The system acetamide—hydroquinone. With reference to this system, Kremann and Auer obtained 3 points [4]. We studied the fusibility and also the viscosity, density and electrical conductivity of various compositions of this system at 135, 145 and 155°. Hydroquinone melts at 171°.

In Fig. 7 the fusibility curve is illustrated and consists of three crystallization branches; two — for the pure components and one — an incongruently melting compound. The eutectic point at 83 mol. % acetamide and 65°, transition point at 50 mol. % acetamide and 100°. Viscosity isotherms (Fig. 8) suddenly rise from the viscosity of acetamide and have a slight convexity to the composition axis. Density isotherms (Fig. 8) are slightly convex from the composition axis. Electrical conductivity isotherms (Fig. 7) as for the previous system, are convex to the composition axis.

Systems with nitrophenols were studied by us only with reference to fusibility. It should be mentioned that the systems acetamide—o-, m- and p-nitrophenol were studied only very superficially (at 3 points), by Kremann and Auer [6]. Purification of the components was as described previously [7]. The melting point of o-nitrophenol was 44.3°, m-nitrophenol 96.4°, p-nitrophenol 113.2°, 2,4-dinitrophenol 114.7°, 2,4,6-dinitrophenol 121.8°.

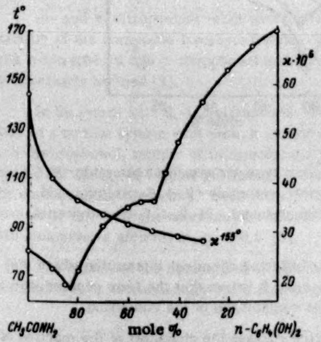

Fig. 7. Fusion and electrical conductivity of the system acetamide—hydroquinone.

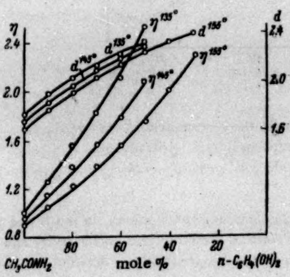

Fig. 8. Density and viscosity of the system acetamide—hydroquinone.

System acetamide – o-nitrophenol. Fusibility curve (Fig. 9) has 2 crystallization branches of the pure components. A eutectic point at 15 mol. % acetamide and 39.5°.

System acetamide – m-nitrophenol. Fusibility curve (Fig. 9) has 3 branches: two crystallization branches of the pure components and a branch – congruent melting compound $CH_3CONH_2 \cdot m\text{-}C_6H_4NO_2(OH)$ m. p. 43.1°. Eutectic points at 69 and 38.5 mol. % acetamide and 47 and 47.8°.

System acetamide – p-nitrophenol. Fusibility curve (Fig. 9) has 3 crystallization branches, melting point of congruent melting compound 95°. Eutectic points at 87 and 29 mol. % acetamide and 65 and 78°. The composition of the compound corresponds to the formula

$$CH_3CONH_2 \cdot p\text{-}C_6H_4NO_2(OH).$$

System acetamide – 2, 4-dinotrophenol. Fusibility curve (Fig. 10) consists of two crystallization branches of the pure components. Eutectic point of composition 76 mol. % acetamide, m. p. 60°.

System acetamide – 2, 4, 6-trinitrophenol (Fig. 10) has 3 crystallization branches: two – of the pure components, and one incongruently melting compound. Eutectic point at 79 mol. % acetamide and 39° and transition point at 56.5 mol. % acetamide and 68.8°.

It should be mentioned that we did not succeed in obtaining acetamide picrate [8] described in the literature, m. p. 117.8°. From saturated aqueous solutions, picric acid comes down. From saturated alcoholic solutions, yellow prismatic crystals come down which decompose above 287°. They may be recrystallized from water without decomposition.

DISCUSSION OF RESULTS

In the system acetamide – phenol, there was established formation of the compound $CH_3CONH_2 \cdot 2C_6H_5OH$ by the fusibility method. Formation of a compound of similar composition was established by fusion, for the system urea – phenol; however, this compound is dissociated so much in the liquid phase that it is not reflected in the viscosity and electrical conductivity curves [2].

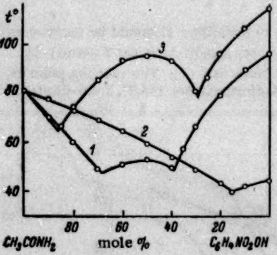

Fig. 9. Fusion in the system acetamide – o-, m- and p-nitrophenol. 1) m-Nitrophenol, 2) o-nitrophenol, 3) p-nitrophenol.

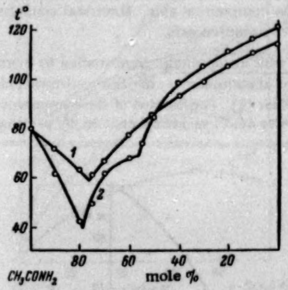

Fig. 10. Density of the systems acetamide – 2, 4-dinitrophenol, acetamide – 2, 4, 6-trinitrophenol. 1) 2, 4-Dinitrophenol, 2) 2, 4, 6-trinitrophenol.

In the system acetamide – phenol, in the liquid phase, there is reflected chemical interaction which may be seen in the form of the electrical conductivity and density isotherms. It is true that the form of these isotherms does not offer the possibility of drawing conclusions about the composition of the compound.

Introduction of a phenolic hydroxyl group into the ortho-position changes the character of the reaction of pyrocatechol and acetamide. On the fusibility curve the formation of an incongruently melting compound is reflected, on whose composition we find it difficult to pass judgment. In all probability in the compound with one molecule of pyrocatechol, no less than 3 molecules of acetamide are attached. Judging by the form of the viscosity, density and electrical conductivity isotherms, the chemical interaction between the components is located in the liquid phase. It is interesting that urea forms a congruent melting compound of composition 1:1, with pyrocatechol and, in spite of the very much higher temperature of the investigation carried out in the liquid phase, this compound was found to be reflected in the viscosity and electrical conductivity curves [2].

In the system acetamide−resorcinol in the region from 70 to 40 mol. % acetamide, a crystalline mixture is not formed. It may be that if crystallization was possible in this field, then the fusibility curve would reflect interaction just as in the previous and later systems. Unfortunately a suffuciently definite confirmation of this suggestion was not obtained on a study of the given system in the liquid phase. Chemical interaction was not reflected in the electrical conductivity isotherms. Extremely remarkable viscosity isotherms which are convex to the composition axis at low temperatures, straighten out with increasing temperature and the 115° isotherm also has a slight positive deviation from the straight line. This circumstance permits us to think that in the liquid phase two processes proceed simultaneously − dissociation of the associated component and interaction between the components. At very low temperatures, there is a reflection of the first process on the viscosity curves and at very high temperatures, a reflection of the second.

With some confirmation of interaction between the components, we may judge the positive density isotherms.

In the system acetamide−hydroquinone;the incongruently melting compound is reflected on the fusibility curve for which one molecule of acetamide is associated with not less than one molecule of hydroquinone. In the liquid phase, interaction is only reflected in the density curves. As in the preceding system, urea forms a more stable compound with hydroquinone than with acetamide and this is stable in the liquid phase [9, 10].

It should be mentioned that if interaction of urea with diatomic phenols takes place, with introduction of a second hydroxyl group this would increase the extent of the chemical reactivity and in the case of acetamide this is impossible.

On introducing nitro groups into the phenol molecule, the mobility of the hydrogen−hydroxyl group must result in increasing chemism on reaction with acetamide, and this is whown by the hydrogen acceptor. However, it has been shown that decomposition of the hydroxyl and nitro groups has a great effect on the character of the interaction.

Thus, in the system acetamide−o-nitrophenol, we did not succeed in reflecting the interaction. In all probability this was linked with the fact that hydrogen of the hydroxyl group of o-nitrophenol is already linked intramolecularly with a hydrogen bond.

m- and p-nitrophenols react with acetamide with formation of a compound composition 1:1. The stability of the compound increases from m- to p-nitrophenol. It is interesting that urea gives layer formation with o-nitrophenol and p-nitrophenol and, like acetamide, forms a compound of composition 1:1, however it is less clearly defined [7].

In ths sytem with 2, 4-dinitrophenol, we did not succeed in reflecting chemical interaction, at the same time in a similar system with urea, a compound is formed [7]. It is evident that on reaction of urea with 2, 4-dinitrophenol, rupture of intramolecular hydrogen bonds takes place, at the same time in the case of acetamide, the energy of rupture of intramolecular hydrogen is concerned more than the energy of formation of the corresponding compound. Even introduction of a third nitro group in the molecule of 2, 4, 6-trinitrophenol resulted in only a slight reaction with acetamide, as in this case an incongruently melting compound is formed; like urea,gives a picrate, m; p. 150.0° [7].

The results of the comparison of interaction of acetamide and urea with nitrophenols may be due to the fact that urea is more strongly basic than acetamide.

SUMMARY

1. Fusibility, viscosity, density and electrical conductivity have been studied of systems formed by acetamide with phenol, pyrocatechol, resorcinol, hydroquinone and fusibility systems of acetamide and o-, m- and p-nitrophenol, 2, 4-dinitrophenol, 2, 4, 6-trinitrophenol.

2. The presence of chemical interaction in the system acetamide – phenol, has been established, with formation of the compound $CH_3CONH_2 \cdot 2C_6H_5OH$.

3. The presence of chemical interaction has been established in the systems acetamide with pyrocatechol, resorcinol and hydroquinone.

4. Chemical interaction was not detected in the systems acetamide with o-nitrophenol, 2, 4-dinitrophenol.

5. Chemical interaction has been established in the systems acetamide with m- and p-nitrophenol and 2, 4, 6-trinitrophenol. The congruently melting compounds

$$CH_3CONH_2 \cdot m\text{-}C_6H_4NO_2(OH) \text{ and } CH_3CONH_2 \cdot p\text{-}C_6H_4NO_2(OH).$$

have been detected.

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Rostov-on-Don State University

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PHYSICOCHEMICAL ANALYSIS OF BINARY SYSTEMS FORMED BY ACETAMIDE WITH ORGANIC ACIDS

III. DENSITY, VISCOSITY AND ELECTRICAL CONDUCTIVITY OF THE SYSTEM ACETAMIDE–TRICHLOROACETIC ACID

Yu. I. Bokhovkina and I. M. Bokhovkin

The present work contains the results of an experimental study of density, viscosity and specific electrical conductivity in the system acetamide–trichloroacetic acid and is a continuation of the systematic investigation of reactions of components of binary systems formed by acetamide with organic acids.

Earlier [1] it was shown that introduction of an atom of chlorine into the acetic acid radical brings about a marked intensification of the chemical interaction of the latter with acetamide. Naturally, it was to be expected that trichloroacetic acid – a product, in the radical of which hydrogen has been substituted by chlorine – would react more vigorously with acetamide.

The system acetamide–trichloroacetic acid was studied by V. L. Albansky [2] by the thermal method. The fusibility curve obtained by him is represented in the lower part of Fig. 1. In the system two chemical compounds are formed of composition 1:1 and 1:2 both with a definite maximum, at 26 and 29.3° and three eutectic points: 1) at 64.12% acetamide and 14.0°; 2) at 41.7% acetamide and 20.6°; 3) at 24.2% acetamide and 22.3°.

In the present investigation the density, viscosity and specific electrical conductivity were measured by the method described in the work [3]. Purification of acetamide was carried out by recrystallization from ether and trichloroacetic acid was purified by distillation, with final extraction in an desiccator over sulfuric acid. The solutions were prepared by weighing and the composition is expressed in molecular percentages. The measurements were carried out at 50, 60 and 70°.

The results of the density measurements are given in Table 1 and represented in the composition – properties diagram (Fig. 1). The density isotherms are illustrated by their own curves with a slight convexity to the composition axis. The results of the viscosity measurements are seen in Table 2 and are illustrated in Fig. 1. The viscosity isotherms have a miximum at 50° and 65% trichloroacetic acid. With increasing temperature, up to 60°, the viscosity is levelled out and displaced to the trichloroacetic acid side. A similar characteristic of the viscosity curves is in accordance with the existing interpretation [4], indicating chemical interaction in the system.

The specific electrical conductivity measurements are given in Table 3 and in Fig. 1.

All the conductivity isotherms have maxima which are displaced slightly to the acetamide side with increasing temperature. Apart from this, all the electrical conductivity isotherms have an inflection corresponding to 50% acetamide. Another inflection is noted at about 70% trichloroacetic acid. We link these inflections with the existence in the homogeneous medium of compounds reflected in the fusibility diagram and corresponding to the component proportions of 1:1 and 1:2.

TABLE 1

Density in the System Acetamide–Trichloroacetic Acid

Content (mole %)		Density		
CH_3CONH_2	CCl_3COOH	50°	60°	70°
70	30	1.061	1.059	1.057
68	32	1.064	1.062	1.060
62	38	1.073	1.070	1.068
60	40	1.075	1.073	1.070
55	45	1.083	1.080	1.078
50	50	1.089	1.086	1.084
45	55	1.094	1.091	1.089
40	60	1.099	1.097	1.094
38	62	1.101	1.098	1.097
35	65	1.103	1.100	1.098
30	70	1.108	1.105	1.103
28	72	1.109	1.107	1.105
25	75	1.111	1.109	1.107

TABLE 2

Viscosity in the System Acetamide–Trichloroacetic Acid

Content (mole %)		Viscosity		
CH_3CONH_2	CCl_3COOH	50°	60°	70°
70	30	11.40	6.57	4.18
68	32	11.64	6.67	4.37
62	38	12.55	7.22	4.45
60	40	12.87	7.35	4.56
55	45	13.51	7.74	4.81
50	50	14.11	8.14	5.05
45	55	14.77	8.57	5.25
40	60	15.33	8.99	5.41
38	62	15.34	9.12	5.47
35	65	15.38	9.24	5.45
30	70	14.82	9.44	5.26
28	72	14.37	9.31	5.15
25	75	13.62	9.08	4.90

TABLE 3

Electrical Conductivity in the System Acetamide–Trichloroacetic Acid and of Reduced Electrical Conductivity at 60°

Content (mole %)		Electrical conductivity $\kappa \cdot 10^4$			$\kappa \cdot 10^3$ at 60°
CH_3CONH_2	CCl_3COOH	50°	60°	70°	
70	30	13.8	18.6	26.0	12.22
68	32	13.8	19.0	26.4	12.67
62	38	14.0	19.1	26.5	13.79
60	40	14.0	19.2	25.9	14.11
55	45	13.7	18.6	24.9	14.39
50	50	13.4	17.8	24.3	14.48
45	55	13.4	17.4	24.1	14.92
40	60	13.6	17.3	23.9	15.55
38	62	13.8	17.3	23.8	15.77
35	65	13.9	17.2	23.7	15.89
30	70	13.9	17.0	22.9	16.04
28	72	14.0	16.7	22.3	15.54
25	75	13.4	15.9	21.0	14.43

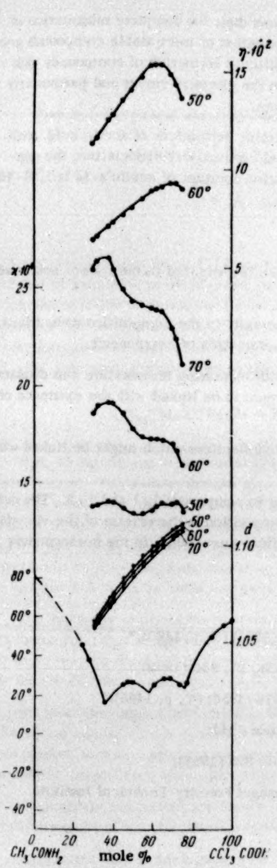

Fig. 1. Fusibility (below), density (d), electrical conductivity (κ) and viscosity (η) in the system acetamide–trichloroacetic acid.

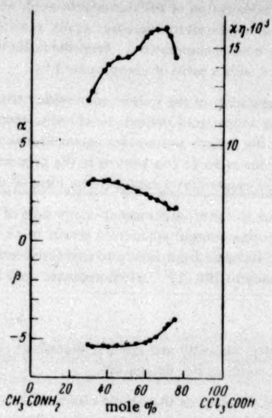

Fig. 2. Reduced electrical conductivity (κη) and temperature coefficients of electrical conductivity (α) and viscosity (β) in the system acetamide–trichloroacetic acid.

The viscosity and electrical conductivity temperature coefficients were calculated (by the formula indicated in the work [3]). The data are represented in Table 4 and Fig. 2. The curve showing relationship between electrical conductivity temperature coefficient and composition is the reverse of the course of the curve for the viscosity temperature coefficient.

TABLE 4

Temperature Coefficients of Electrical Conductivity (α) and Viscosity (β)

Content (mole %)		α	β
CH_3CONH_2	CCl_3COOH	50–60°	50–60°
70	30	2.96	—5.36
68	32	3.17	—5.41
62	38	3.08	—5.38
60	40	3.13	—5.46
55	45	3.03	—5.42
50	50	2.82	—5.28
45	55	2.59	—5.27
40	60	2.39	—5.21
38	62	2.25	—5.10
35	65	2.12	—4.97
30	70	2.00	—4.44
28	72	1.76	—4.25
25	75	1.70	—4.01

In order to study the influence of viscosity on electrical conductivity, we calculated the reduced electrical conductivity (Table 3, Fig. 2), the curve not differing very much from the usual one, with composition. At first it rises with concentration of trichloroacetic acid, at 50% acetamide there is a sudden inflection, then the course of the electrical conductivity increases again, reaches a maximum and suddenly falls with further increase in trichloroacetic acid concentration. From the inflection in the electrical conductivity curve, we consider a compound is formed with a ratio of components 1 : 1.

An investigation of the system acetamide – trichloroacetic acid shows that, for complete substitution of hydrogen in the acetic acid radical, by chlorine atoms, the process of formation of more stable compounds goes further than in the system acetamide – monochloroacetic acid. The stability of formation of compounds with components in the ratio 1 : 1 as well as in the proportion 1 : 2, is shown in the viscosity curves and particularly in the electrical conductivity curves in the form of more abrupt inflections.

Increasing stability of chemical compounds of acetamide with chlorine derivatives of acetic acid, with increase in chlorine content apparently results in an increase in electrical conductivity dissociation, the constants of which increase from acetic to trichloroacetic acid: the dissociation constant of acetic acid is $1.86 \cdot 10^{-5}$, of monochloroacetic $160 \cdot 10^{-5}$, trichloroacetic acid $30{,}000 \cdot 10^{-5}$ [4].

SUMMARY

1. Density, viscosity and specific electrical conductivity have been investigated in the system acetamide – trichloroacetic acid, at 50, 60 and 70°.

2. Density isotherms show their own specific curve with slight convexity to the composition axis, illustrated by the course of the system discussed, apparently linked with chemical interaction of components.

3. Viscosity isotherms have a maximum which is smoothed out with increasing temperature and displaced to the side of trichloroacetic acid. We consider formation of this maximum to be linked with the existence of the compound 1 : 2.

Viscosity temperature coefficient curves do not form characteristic inflections which might be linked with the presence of compounds.

4. Electrical conductivity isotherms have inflections corresponding to compounds 1 : 1 and 1 : 2. The curve for dependence of electrical conductivity temperature coefficient on composition is the reverse of the viscosity temperature coefficient curve and does not indicate the existence of definite compounds in the homogeneous melt.

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THE REACTION OF POTASSIUM FLUOBORATE WITH STYRYLMAGNESIUM AND PHENYLACETYLENYLMAGNESIUM BROMIDES

V.A. Sazonova and N.Ya. Kronrod

A.N. Nesmeyanov et al. [1] investigated the reaction of KBF_4 with various organomagnesium compounds and found that this reaction resulted either in tetraarylboron salts or in trialkyl- or triarylboron. It seemed interesting to study the reaction of potassium fluoborate with unsaturated organomagnesium compounds. We selected styrylmagnesium and phenylacetylenylmagnesium bromides as examples. Styrylmagnesium bromide reacted with KBF_4 with the formation of styrylboric acid. In analogy with previously examined reactions it seemed likely that in this case, also, potassium tetrastyrylboron would be formed and decompose into styrylboric acid:

$$C_6H_5CH{=}CHMgBr + KBF_4 \rightarrow [KB(CH{=}CHC_6H_5)_4] \xrightarrow[O_2]{H_2O} C_6H_5CH{=}CHB(OH)_2.$$

N.N. Melnikov and M.S. Rokitskaya [2] obtained this acid by the reaction of styrylmagnesium bromide with isobutyl borate. The authors did not give the yield of styrylboric acid; they characterized it as being a colorless crystalline substance with m.p. 138-141° (with partial decomposition), very easily decomposed and yellowing even on storage in the dark. This data does not correspond with our findings: styrylboric acid purified by recrystallization from water was quite stable and could be kept in a closed vessel for a long time without change. The tendency of styrylboric acid to dehydrate should be noted among its other properties. On being dried in a vacuum desiccator over P_2O_5 for 4-5 hours the acid was partially converted into the anhydride.

The tendency of organoboric acids to dehydrate had previously been described by Michaelis [3] who prepared phenylboric and other anhydrides. The process of anhydride formation is considerably accelerated by heating [4]. Anhydrides may be obtained in a pure form by prolonged heating of the corresponding acid above the melting point or by the use of dehydrating agents (P_2O_5 [5], conc. H_2SO_4 [3], $CaSO_4$ [6] and $SOCl_2$ [7]).

We used anhydrous ferric chloride for the dehydration of styrylboric acid. Anhydride formation started immediately on adding a saturated ether solution of $FeCl_3$ to an ether solution of styrylboric acid. This method required neither vacuum apparatus nor prolonged heating. The styrylboric anhydride obtained was a colorless substance which crystallized from ether as needles with m.p. 149-151°.

Organoboric anhydrides are known [8] to exist in the di- and trimer form. Cryoscopic determination of the molecular weight of the styrylboric anhydride in nitrobenzene solution showed that it existed in the dimer form.

Styrylboric acid is analogous in its chemical properties to arylboric acids. Thus, for example, on being heated for 20 minutes with mercuric chloride in acetone solution, it quantitatively gave styrylmercuric chloride:

$$C_6H_5CH{=}CHB(OH)_2 \xrightarrow{HgCl_2} C_6H_5CH{=}CHHgCl,$$

while alkylboric acids dealkylate under much more drastic conditions and the reaction does not proceed quantitatively. Thus n-propylmercuric chloride was obtained in 55% yield by heating n-propylboric acid [9] in aqueous solution at 140-150° with mercuric chloride.

Furthermore, on being boiled for a short time in aqueous solution with thallium trichloride, styrylboric acid, like arylboric acids [2,9], gave distyrylthallium chloride in 84% yield:

$$2C_6H_5CH{=}CHB(OH)_2 \xrightarrow{TlCl_3} (C_6H_5CH{=}CH)_2TlCl.$$

Hence the similarity of the chemical properties of styrylboric acid to those of arylboric acids furnishes another example in the study of vinyls.

In contrast to the reaction of potassium fluoborate with styrylmagnesium bromide described above, phenylacetylenylmagnesium bromide reacted with KBF_4 with the formation of ammonium tetraphenylacetylenylboron:

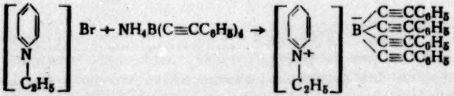
$$C_6H_5C{\equiv}CMgBr + KBF_4 \rightarrow [KB(C{\equiv}CC_6H_5)_4] \xrightarrow{NH_4Cl} NH_4B(C{\equiv}CC_6H_5)_4.$$

It seems likely that here also the potassium salt is formed first and is converted by NH_4Cl into the ammonium salt. The latter crystallizes from water as a crystal hydrate (with one molecule of water). The compound is less heat-stable than potassium tetraphenylboron and potassium tetra-(p-tolyl)-boron and darkens when heated to 212-220°.

Ammonium tetraphenylacetylenylboron in an alcohol solution was decomposed almost quantitatively by ammoniacal cuprous chloride solution with the formation of yellow copper phenylacetylide. An alkaline solution of mercuric iodide decomposed ammonium tetraphenylacetylenylboron to give diphenylacetylenylmercury, the yield of which (as well as that of copper phenylacetylide) confirmed the presence in this salt of four phenylacetylene groups.

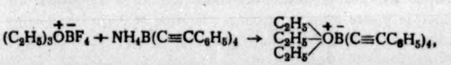
Like other tetraarylboron salts investigated, ammonium tetraphenylacetylenylboron has the properties of a typical salt: it is soluble in hot water and alcohol, insoluble in benzene and carbon tetrachloride and undergoes ion exchange reactions easily.

Thus N-ethylpyridine tetraphenylacetylenylboron was obtained in 97% yield by combining alcohol solutions of ammonium tetraphenylacetylenylboron and N-ethylpyridine bromide:



This salt is a colorless substance which decomposes at 180-190°, crystallizes from alcohol as needles, is easily soluble in acetone, nitromethane and nitrobenzene, and is insoluble in ether and benzene.

The reaction of aqueous solutions of ammonium tetraphenylacetylenylboron and freshly prepared triethyloxonium fluoborate produced triethyloxonium tetraphenylacetylenylboron:



$$(C_2H_5)_3\overset{+\,-}{O}BF_4 + NH_4B(C{\equiv}CC_6H_5)_4 \rightarrow (C_2H_5)_3\overset{+\,-}{O}B(C{\equiv}CC_6H_5)_4,$$

which is a colorless crystalline substance with m.p. 58-62° (with decomp.), soluble in nitromethane and nitrobenzene and insoluble in water, ether and benzene. In contrast to the rather stable triethyloxonium tetraphenylboron (m.p. 115-116°), triethyloxonium tetraphenylacetylenylboron is extremely unstable, decomposing completely several hours after formation. Like other oxonium salts, this salt has the power of alkylation. Dissolving it in pyridine by heating resulted in the formation of N-ethylpyridine tetraphenylacetylenylboron.

EXPERIMENTAL

Styrylboric acid. A solution of 25g of ω-bromostyrene in 10 ml of absolute ether was slowly added with vigorous stirring to an ether suspension of 17.2 g of KBF_4 and 4.98 g of magnesium in 60 ml of absolute ether.

When the reaction began a further 40 ml of ether was added to the reaction mixture. After the addition of all the ω-bromostyrene the reaction mixture was stirred for one hour and then was poured into ice cooled dilute (1 : 10) acetic acid and unreacted magnesium was filtered off. The ether layer was separated, washed with water and then was treated four times with 2 N NaOH. The combined alkaline extracts were washed with ether and were acidified with ice cold conc. HCl; styrylboric acid was thus precipitated. After standing in ice for four hours the precipitate was filtered off, washed with water, and dried. The mother liquor was extracted with ether. The ether was evaporated and the residue was styrylboric acid. Yield 1.28 g (25%) of styrylboric acid. The material was recrystallized from water (part of the acid being hydrolyzed), dried over 60% H_2SO_4: m.p. 129° determined in a sealed capillary lowered into a preheated apparatus.

Found %: B 7.32. $C_8H_9BO_2$. Calculated %: B 7.31.

Styrylboric acid is a colorless crystalline substance, stable when kept in a closed vessel. On prolonged drying in a vacuum desiccator over P_2O_5 the acid was partially dehydrated; it was readily soluble in ether and acetone, with difficulty in cold benzene, petroleum ether and cold water.

Styrylmercury chloride. A solution of 0.2 g of styrylboric acid in acetone mixed with a solution of 0.74 g of mercuric chloride in acetone was heated for 20 minutes and then poured into water. The precipitate was filtered off, carefully washed with water, and dried. Yield 0.44 g (100%) of styrylmercury chloride with m.p. 214°. After recrystallization from alcohol-acetone, m.p. 216.5-217.5°.

Literature data: m.p. 218° [10].
Found %: C 28.54, 28.44; H 2.24, 2.21. C_8H_7HgCl. Calculated %: C 28.32; H 2.08.

Distyrylthallium chloride. 0.47 g of styrylboric acid was dissolved in 25 ml of water by heating. To the clear solution was added an aqueous solution of 0.49 g of thallium trichloride. A voluminous white precipitate separated out immediately. The reaction mixture was heated to boiling, then it was cooled and the precipitate of distyrylthallium chloride was filtered off, washed with water and dried. Yield 0.59 g (84%) $(C_6H_5CH=CH)_2TlCl$. After recrystallization from pyridine m.p. 254° (with decomp.).

Literature data: m.p. 253° (with decomp.) [10].
Found %: C 42.96, 42.75; H 3.27, 3.46. $C_{16}H_{14}TlCl$. Calculated %: C 43.07; H 3.16.

Dehydration of styrylboric acid. 0.2 g of styrylboric acid was dissolved in the minimum amount of ether. To the clear solution was added a saturated ether solution of anhydrous ferric chloride until crystals appeared. The reaction mixture was vigorously shaken several times. The precipitate was filtered off, washed with ether and dried in a vacuum desiccator over P_2O_5. Yield 0.09 g (47%) of styrylboric anhydride with m.p. 149-151°.

The ether was evaporated from the filtrate; the residue was washed with water until there was a negative reaction for ionic iron, dried, and used again for the preparation of the anhydride.

Styrylboric anhydride is a colorless crystalline substance, readily soluble in acetone and alcohol, difficultly soluble in ether and dissolves in water only upon heating.

Found %: B 8.23. C_8H_7BO. Calculated %: B 8.32.
M (in nitrobenzene) 256. $C_{16}H_{16}B_2O_2$. Calculated M 259.8.

Ammonium tetraphenylacetylenylboron. 6 g of phenylacetylene was added to an ether solution of ethylmagnesium bromide obtained from 7 g of ethyl bromide and 1.4 g of magnesium. The reaction mixture was heated on a water bath for two hours. Then 1.82g of potassium fluoborate was added to it and heating was continued for 1.5 hours with vigorous stirring; after this the reaction mixture was cooled and poured into a saturated solution of NH_4Cl. At the boundary of the water and ether layers a white precipitate was formed. The ether layer, together with the precipitate, was treated with a concentrated ammonia solution (the precipitate was slightly increased by this) and was separated off. The precipitate was filtered off, washed with water and ether, and dried. Yield 1.84 g (27%) of ammonium tetraphenylacetylenylboron. The material was recrystallized from water (an insignificant amount being hydrolyzed). The crystalline hydrate obtained contained one molecule of water of crystallization, $NH_4B(C\equiv CC_6H_5)_4 \cdot H_2O$. This colorless crystalline material was readily soluble in alcohol, acetone and dioxane; difficultly soluble in ether and cold water; insoluble in benzene and petroleum ether.

Found %: C 85.09, 85.12; H 6.05, 5.88; B 2.30, 2.13; N 2.93, 2.91. $C_{32}H_{26}BNO$. Calculated %: C 85.16; H 5.80; B 2.39; N 3.10.

Decomposition of ammonium tetraphenylacetylenylboron with an ammonia solution of cuprous chloride. A solution of 0.1532 g of ammonium tetraphenylacetylenylboron in 5 ml of alcohol was added with vigorous shaking to 20 ml of an ammonia solution of cuprous chloride prepared by Hein and Meyer's method from 0.3 g of $CaCl_2$, 1 g of hydroxylamine hydrochloride, 0.48 g of NH_4Cl, 0.5 ml of conc. NH_4OH and 19.5 ml of water. Over several minutes a yellow precipitate of copper phenylacetylide formed, which was filtered off, washed with water, alcohol and ether, and dried to constant weight. Yield 0.2195 g (98.16%) of copper phenylacetylide.

Decomposition of ammonium tetraphenylacetylenylboron with mercuric iodide. To an alkaline mercuric iodide solution, prepared from 0.63 g of mercuric chloride, 1.65 g of KI, 1.6 ml of water and 1.2 ml of 10% NaOH, a solution of 0.23 g of ammonium tetraphenylacetylenylboron in 6 ml of ethyl alcohol was added dropwise. Immediately a precipitate came down, which was filtered off, washed with 50% alcohol, and dried. Yield 0.40 g (97.6%) of diphenylacetylenylmercury. After recrystallization from alcohol, m.p. 123.5-124.5°.

Literature data: m.p. 125° [12].

N-Ethylpyridine tetraphenylacetylenylboron. To an alcohol solution of 0.63 g of ammonium tetraphenylacetylenylboron was added excess alcohol solution of N-ethylpyridine bromide. Immediately a voluminous white precipitate came down, which was filtered off, washed with water and alcohol and dried. Yield 0.71 g (97%) of N-ethylpyridine tetraphenylacetylenylboron, which was a colorless material crystallizing from alcohol as needles with decomposition point 180-190°. The material turned yellow in light, could be stored for a long time in darkness, and was readily soluble in acetone, nitromethane, and nitrobenzene; it was insoluble in water, cold alcohol and ether.

Found %: C 88.96, 89.26; H 5.85, 5.72; B 2.16, 2.11; N 2.74, 2.59. $C_{39}H_{29}BN$. Calculated %: C 89.05; H 5.59; B 2.07; N 2.68.

Triethyloxonium tetraphenylacetylenylboron. 0.4 g of ammonium tetraphenylacetylenylboron was dissolved in 80 ml of water by heating. The solution was filtered hot into a freshly prepared solution of 0.5 g of triethyloxonium fluoborate in 100 ml of water, cooled in an ice-salt mixture. Immediately a white precipitate was formed, which was filtered off, washed with water and ether, and dried. Yield 0.27 g (59%) of triethyloxonium tetraphenylacetylenylboron.

For purification the material was dissolved in nitromethane and was precipitated by the addition of ether. Colorless crystals were obtained with m.p. 58-62° (with decomp.). The material was readily soluble in nitromethane, acetone and chloroform; it was insoluble in water,ether and benzene. It was extremely unstable, quickly turned yellow, and after a few hours completely decomposed.

Found %: C 87.37; H 6.82; B 1.78. $C_{38}H_{35}BO$. Calculated %: C 88.02; H 6.80; B 2.08.

Alkylation of pyridine with triethyloxonium tetraphenylacetylenylboron. To 0.1 g of triethyloxonium tetraphenylacetylenylboron was added 3 ml of pyridine. The salt dissolved in the pyridine on warming. The solution was heated at 60° for several minutes and then water was added to it to precipitate the N-ethylpyridine tetraphenylacetylenylboron. The precipitate which separated was filtered off and washed with water and ether. Yield 0.09 g (90%). The material was recrystallized from alcohol. The salt obtained was identical in its properties with that described above, it was easily soluble in nitrobenzene, nitromethane and acetone; insoluble in water, ether and benzene. M.p. 180-190°.

Found %: N 2.80, 2.84. $C_{39}H_{29}BN$. Calculated %: N 2.68.

SUMMARY

1. Styrylboric acid was prepared by the reaction of potassium fluoborate with styrylmagnesium bromide. Its properties were investigated.

2. The reaction of potassium fluoborate with phenylacetylenylmagnesium bromide with subsequent decomposition of the reaction mixture with ammonium chloride solution gave ammonium tetraphenylacetylenylboron. By exchange reactions of the latter with N-ethylpyridine bromide and triethyloxonium fluoborate, N-ethylpyridine tetraphenylacetylenylboron and triethyloxonium tetraphenylacetylenylboron, respectively, were prepared.

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Moscow State University

OXONIUM COMPOUNDS OF COMPLEX ETHERS WITH ORGANIC ACIDS

III. THE SYSTEMS $HCOOC_2H_5-CH_3COOH$ AND $CCl_3COOC_2H_5-CH_3COOH$

M. Usanovich, K. Bilyalov and L. Krasnomolova

Continuing the investigation of oxonium properties of complex ethers [1,2], we carried out viscosity and density measurements on the system

$$HCOOC_2H_5-CH_3COOH$$

and viscosity, density and vapor pressure measurements on the system

$$CCl_3COOC_2H_5-CH_3COOH.$$

The preparations had the following constants: ethyl formate b.p. 52° (688 mm), ethyl trichloroacetate b.p. 164° (691 mm) and acetic acid m.p. 16.67°.

The viscosity and density of the system $HCOOC_2H_5-CH_3COOH$ were determined at 25, 40 and 60°. The results of the measurements are given in Table 1.

We were unable to carry out measurements on the properties of mixtures with more than 70 mole % of ethyl formate at 60°, as at this temperature the mixtures boiled.

TABLE 1

The System $HCOOC_2H_5-CH_3COOH$

Percentage ether		Viscosity (in centipoises)			Density		
Mol.	Weight	25°	40°	60°	25°	40°	60°
0.00	0.00	1.118	0.905	0.694	1.0442	1.0279	1.0074
10.07	12.15	0.975	0.795	0.624	1.0267	1.0095	0.9893
20.36	23.98	0.846	0.695	0.554	1.0080	0.9913	0.9708
30.00	34.61	0.755	0.627	0.507	0.9939	0.9773	0.9550
40.34	45.49	0.664	0.554	0.461	0.9785	0.9617	0.9415
49.79	55.03	0.608	0.512	0.424	0.9649	0.9491	0.9269
59.78	64.72	0.550	0.466	0.392	0.9525	0.9356	0.9131
69.63	73.89	0.505	0.432	0.365	0.9384	0.9226	0.8974
80.01	83.16	0.459	0.391	—	0.9251	0.9095	—
89.41	91.25	0.424	0.362	—	0.9166	0.8994	—
95.03	95.93	0.395	0.340	—	0.9004	0.8924	—
100.00	100.00	0.378	0.322	—	0.9040	0.8842	—

A diagram of the viscosity and specific volume is given in Fig. 1. The viscosity isotherms are slightly convex toward the composition axis along their whole extent. The specific volume isotherms indicate that there is slight contraction in the system.

If we follow the distribution of points on the viscosity isotherms starting from acetic acid, there is noticeable difficulty in drawing a smooth curve around to the points showing the viscosity of ethyl formate. As a result of this we plotted log η against composition and were convinced that the curves showed a definite inflection (Fig. 1). In our opinion, this indicates the presence of reaction between the components, since for systems which do not react, such plots gave us either curves which are smooth along their whole length, or straight lines.

The density, viscosity and vapor pressure of the system $CCl_3COOC_2H_5-CH_3COOH$ were determined. The results of density and viscosity measurements are listed in Table 2 and are shown graphically in Fig. 2.

TABLE 2

The System $CCl_3COOC_2H_5-CH_3COOH$.

Percentage ether		Viscosity (in centipoises)			Density		
Mol.	Weight	25°	40°	60°	25°	40°	60°
0.00	0.00	1.118	0.905	0.694	1.0442	1.0279	1.0074
4.99	14.38	1.073	0.867	0.675	1.0750	1.0580	1.0380
7.05	19.49	1.068	0.865	0.672	1.0897	1.0734	1.0526
9.99	26.13	1.065	0.863	0.658	1.1079	1.0921	1.0696
15.23	36.43	1.078	0.868	0.678	1.1356	1.1201	1.0966
19.91	44.23	1.088	0.880	0.686	1.1611	1.1452	1.1211
32.80	57.62	1.129	0.910	0.709	1.2052	1.1863	1.1639
40.57	68.53	1.198	0.961	0.742	1.2434	1.2259	1.2009
59.38	82.34	1.282	1.025	0.806	1.2947	1.2780	1.2525
76.61	91.27	1.389	1.107	0.857	1.3331	1.3161	1.2908
100.00	100.00	1.585	1.249	0.931	1.3834	1.3644	1.3377

As the diagram shows (Fig. 2), the viscosity isotherms for all the temperatures pass through a minimum. This minimum coincides approximately with 10 mole % of ether; with an increase in temperature the minimum becomes less marked and is shifted toward acetic acid. The minimum is due to the break-up of associated acid molecules by ether.

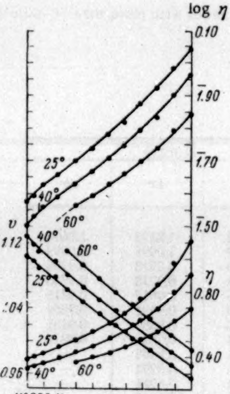

Fig. 1. Viscosity (composition in molecular percentage) and specific volume (composition in weight percentage) of the system $HCOOC_2H_5-CH_3COOH$.

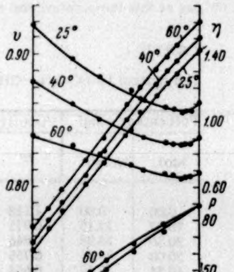

Fig. 2. Viscosity, vapor pressure (composition in molecular percentage) and specific volume (composition in weight percentage) of the system $CCl_3COOC_2H_5-CH_3COOH$.

The viscosity diagram does not indicate chemical reaction, but shows only the break-up of associated acid molecules. The specific volume isotherms (Fig. 2) indicate an insignificant expansion, which is also caused by the dissociation of acetic acid molecules.

The results of vapor pressure measurements are listed in Table 3.

The plot of total and partial vapor pressures against composition (Fig. 2) shows that the partial vapor pressure of the ether has a negative, while that of the acetic acid has a positive, deviation from Raoult's law.

The total vapor pressure deviates positively from the ideal case, although the ethyl trichloroacetate curve indicates the presence of reaction in the system. Apparently this is explained by the fact that the process of dissociation of acid molecules predominates over the reaction process.

The combined data obtained lead to the conclusion that in the system composed of ethyl ether, trichloroacetic acid and acetic acid,reaction between the components takes place which, however, does not show in the viscosity diagram due to the predominance of the process of association of acid molecules.

TABLE 3

Vapor Pressure of the System $CCl_3COOC_2H_5-CH_3COOH$.

Content of $CCl_3COOC_2H_5$ (in mole %)	Temperature (upper figure) and vapor pressure (in mm)					
0.0	41.2 37	44.5 45	60.0 93	64.1 110	74.5 171	83.5 249
20.4	53.5 55	57.5 66	60.0 78	62.5 85	68.0 110	71.3 128
38.4	53.5 49	57.5 57	60.0 66	65.3 81	68.3 94	71.5 108
56.2	46.0 29	54.0 43	60.0 56	64.5 65	68.5 81	72.0 96
65.2	50.3 31	55.5 39	60.0 49	68.0 66	71.5 77	73.5 85
82.4	46.0 17	51.5 24	56.5 30	60.0 34	66.0 44	70.0 52
100.0	60.0 15	69.0 22	73.5 29	79.0 38	84.0 48	

SUMMARY

The viscosity and density of the systems $HCOOC_2H_5-CH_3COOH$ and $CCl_3COOC_2H_5-CH_3COOH$ were determined at 25, 40 and 60°. The vapor pressure of the latter system was also determined. The existence of reaction was established in the system investigated.

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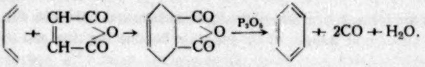
SYNTHESIS OF HYDROCARBONS

LVI. CONVERSION OF HYDROAROMATIC KETONES INTO AROMATIC HYDROCARBONS BY PHOSPHORUS PENTOXIDE

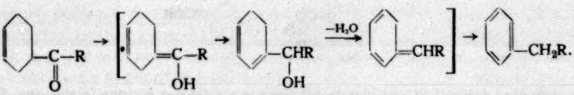
R.Ya. Levina, Kim Dyai Gir and V.R. Skvarchenko

We had previously discovered and investigated [1-4] a new reaction leading to the formation of aromatic hydrocarbons – the action of phosphorus pentoxide on tetrahydrophthalic anhydrides, the adducts of conjugated diene hydrocarbons and maleic anhydride and its homologs:

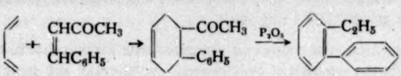


In the present work, reaction with phosphorus pentoxide was used to convert hydroaromatic ketones of various structures (with different positions of the ketone group and double bond) into aromatic hydrocarbons.

Thus, under the action of phosphorus pentoxide, ketones with a Δ^3-cyclohexenyl radical (that is with a double bond in the γ,δ-position to the carbonyl group), which are adducts of conjugated dienes with α,β-unsaturated ketones, undergo keto-enol rearrangement, dehydration, and transfer of the double bond to the ring (the latter process was fully described earlier by one of us [5]), with the formation of aromatic systems: *



The adduct of divinyl with benzalacetone – 5-acetyl-4-phenylcyclohexene-1 – was reacted with phosphorus pentoxide; the reaction product – 2-ethyldiphenyl – was obtained in 22% yield.



The action of phosphorus pentoxide on the adduct of divinyl and p-benzoquinone (bis-butadienequinone) gave a mixture of dihydroanthracenes (19% yield):

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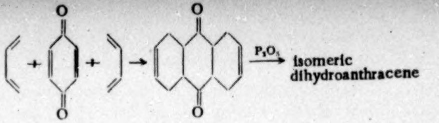
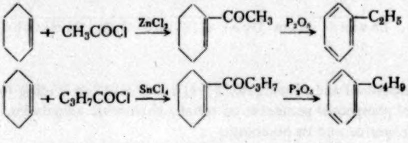
* A.A. Petrov and N.P. Sopov recently described a similar reaction – the dehydration of adducts of dienes with α,β-unsaturated ketones and aldehydes by heating with phosphorus pentoxide [6]; the authors used the same reaction conditions as described by us for tetrahydrophthalic anhydrides and the same treatment of the reaction products (sodium carbonate, water; 80% sulphuric acid and water), but they made no reference to our work.

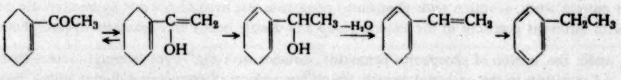


The reaction of phosphorus pentoxide on exocyclic ketones of the cyclohexene series was further investigated using ketones with the double bond in another position in the ring (alkyl-Δ'-cyclohexenyl ketones with the double bond in the α,β-position to the ketone group).

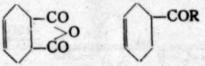
Methyl-Δ'-cyclohexenyl ketone and propyl-Δ'-cyclohexenyl ketone were used; the reaction between these ketones and phosphorus pentoxide gave the corresponding alkylbenzenes (34% yield)



In these reactions the formation of aromatic hydrocarbons was likewise due to keto-enol rearrangement of the original ketone with subsequent transfer of the multiple bond to the ring and dehydration of the alcohol produced, for example:



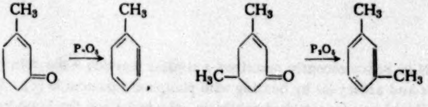
It was thus established that aromatization by phosphorus pentoxide was possible not only for products of "diene synthesis", having a double bond in the γ,δ-position to the carbonyl or carboxyl group



but also for cyclohexene derivatives with the double bond in a different position in the ring, for example, exocyclic ketones with the double bond in the α,β-position to the carbonyl group.

In all the ketones investigated the ketone group was situated in a side chain of the cyclohexene ring. It seemed interesting to investigate further what effect on the aromatization reaction would be produced by a different position of the ketone group – in the ring itself.

We investigated the reaction of phosphorus pentoxide with ketones that had been used in our previous work [7] as the starting materials for the synthesis of cyclohexene, cyclohexane and dicyclohexane hydrocarbons with a quaternary carbon atom, i.e., 1-methylcyclohexen-1-one-3 and 1,5-dimethylcyclohexen-1-one-3, which have a double bond and a ketone group in the six membered ring. It was found that even though ketones with this structure do react, they give only a small yield (6-8%) of the corresponding alkylbenzenes:



EXPERIMENTAL

Action of phosphorus pentoxide on 5-acetyl-4-phenylcyclohexene-1. Phosphorus pentoxide (10.45 g, 0.075 mole) was added to 5-acetyl-4-phenylcyclohexene-1 (15 g, 0.075 mole; obtained by heating benzalacetone with divinyl in an autoclave at 170-180° [8]; m.p. 62-63°); heat was evolved and the temperature rose to 180-200° (thermometer in the reaction mixture). The hydrocarbon was distilled off by further heating to 240° and then was washed successively with sodium carbonate, water, 80% sulfuric acid and again with water until it was neutral, dried with calcium chloride, and distilled over sodium. The 2-ethyldiphenyl obtained (2 g, 22%) had the following constants:

B.p. 105-106° (6 mm), n_D^{20} 1.5798, d_4^{20} 0.9965. Literature data: b.p. 93-94° at 2-3 mm, n_D^{20} 1.5805 [9]; b.p. 265.9 at 760 mm, n_D^{20} 1.5805, d_4^{20} 0.9967 [10].

Action of phosphorus pentoxide on bis-butadienequinone. Bis-butadienequinone (16 g, 0.074 mole; obtained by heating p-benzoquinone with divinyl in an autoclave at 100° [11]; m.p. 154-155°) was gradually heated to 250° in a flask with a curved side-arm. The reaction product (total yield 2 g, 19%) was obtained by distillation of the reaction mixture under vacuum and by recrystallization from alcohol it was separated into anthracene (m.p. 215°; undepressed by admixture with authentic anthracene; picrate m.p. 138°) and lower-melting fractions of crystals with m.p. from 110 to 200°, which, apparently, were mixtures of anthracene and isomeric dihydroanthracenes;* by heating with sulfur they were converted into anthracene with m.p. 215°.

Action of phosphorus pentoxide on methyl-Δ'-cyclohexenyl ketone (1-acetylcyclohexene-1). The reaction between 1-acetylcyclohexene-1 (17 g, 0.14 mole; obtained by acetylation of cyclohexene with acetic anhydride in the presence of zinc chloride [14]; b.p. 85-90° at 15 mm; n_D^{20} 1.4918) and phosphorus pentoxide (20 g, 0.14 mole) was carried out under the same conditions as described for 5-acetyl-4-phenylcyclohexene-1. After working up as described above, ethylbenzene (5 g, 34.5%) was obtained:

B.p. 135° (737 mm), n_D^{20} 1.4952, d_4^{20} 0.8630. Literature data [15]: b.p. 136.2 at 760 mm, n_D^{20} 1.4959, d_4^{20} 0.8670.

Action of phosphorus pentoxide on propyl-Δ'-cyclohexenyl ketone (1-butyrylcyclohexene-1). By the reaction of propyl-Δ'cyclohexenyl ketone (20 g, 0.13 mole; obtained by treating cyclohexene with butyryl chloride in the presence of stannic chloride [16]; b.p. 106-110° at 12 mm; n_D^{20} 1.4852) with phosphorus pentoxide (18 g, 0.13 mole) under the conditions described above, butylbenzene (5.8 g, 34%) was obtained:

B.p. 182-182.5° (751 mm), n_D^{20} 1.4930, d_4^{20} 0.8623. Literature data [17]: b.p. 183.1° at 760 mm, n_D^{20} 1.4936, d_4^{20} 0.8620.

Action of phosphorus pentoxide on 1-methylcyclohexe-1-one-3. Phosphorus pentoxide (25 g, 0.18 mole) was reacted with 1-methylcyclohexen-1-one-3 (18 g, 0.18 mole; obtained by ketonic fission of methylen-bis-acetoacetic ether [18]; b.p. 198-200° at 750 mm, n_D^{20} 1.4887) and after working up as described above and distilling over sodium we obtained a hydrocarbon fraction with b.p. 100-110° (1 g, 6%), which gave on nitration 2,4-dinitrotoluene with m.p. 70° (undepressed by admixture with authentic 2,4-dinitrotoluene).

Action of phosphorus pentoxide on 1,5-dimethylcyclohexen-1-one-3. From the products of the reaction of phosphorus pentoxide (22.7 g, 0.16 mole) and 1,5-dimethylcyclohexen-1-one-3 (20 g, 0.16 mole; obtained by ketonic fission of ethylidene-bis-acetoacetic ether [18]; b.p. 73° at 6 mm, n_D^{20} 1.4848) was separated a hydrocarbon fraction with b.p. 137-141° (747 mm) and n_D^{20} 1.4905 (1.4 g, 8.2%), which gave on nitration 2,4,6-trinitro-m-xylene with m.p. 181-182°. Literature data [19]: m.p. 182°.

SUMMARY

1. It was shown that hydroaromatic ketones of various structures – with the ketone group in and out of the ring and with the double bond in the γ,δ- or α,β-positions to the ketone group – were converted into aromatic hydrocarbons by heating with phosphorus pentoxide.

2. The aromatic hydrocarbons were obtained in various yields, depending on the structure of the parent ketone: hydroaromatic ketones with an α,β-double bond and the ketone group in the ring (1-methylcyclohexen-1-one-3 and 1,5-dimethylcyclohexene-1-one-3) gave aromatic hydrocarbons in 6-8% yield; ketones with the double bond in the same position but the ketone group in a side chain (1-acetylcyclohexene-1 and 1-butyrylcyclohexene-1) gave a 34% yield; 5-acetyl-4-phenylcyclohexene-1 and bis-butadienequinone (ketones with a γ,δ-double bond and the ketone group in a side chain) were converted into the corresponding hydrocar-

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* Literature data for 1,2-dihydroanthracene: m.p. 150° [12]; for 9,10-dihydroanthracene: m.p. 108° [13].

bons in yields of 22 and 19%.

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* T.p. = C.B. Translation pagination

THE PROBLEM OF EXPERIMENTAL PROOF OF THE BAKER-NATHAN EFFECT

M. I. Batuev

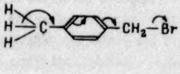
I. In 1935, Baker and Nathan [1] investigated the rate of formation of benzylpyridine bromides by the reaction of pyridine with alkylsubstituted benzylbromides in anhydrous acetone. They based the explanation of their findings on the assumption that these rates increase in proportion to the increasing facility of anionization of the bromine atom in $p\text{-}R-C_6H_4-CH_2Br$ which depends on the nature of the substituent R. At the time a hypothetical positive inductive effect, denoted by the symbol + I had been accepted by the English school and according to it alkyls presumably had the capacity of repelling electrons and could be arranged in the following order with respect to the size of this effect:

$$CH_3 < CH_2CH_3 < CH(CH_3)_2 < C(CH_3)_3.$$

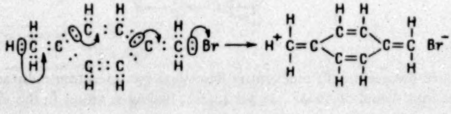
On the basis of this assumed effect, Baker and Nathan expected the rate of the reaction to increase if R in $p\text{-}R-C_6H_4-CH_2Br$ was replaced by alkyls in the above order, that is the reaction rate would be least when $R = CH_3$ and greatest when $R = C(CH_3)_3$. However, when R in $p\text{-}R-C_6H_4-CH_2Br$ was actually replaced by alkyls the rate of the reaction increased in reverse order to that required by the hypothesis of the + I effect, that is it increased anomalously in relation to the effect: the capacity of electron repulsion was found to be $CH_3 > CH_2CH_3 > CH(CH_3)_2 > C(CH_3)_3$.

To explain this anomaly Baker and Nathan proposed another hypothesis on the existence of a second effect in alkyls, besides the + I effect, and this was later named after them. In American literature this effect was called hyperconjugation. The gist of the proposed effect consisted of the following.

Baker and Nathan assumed a situation where an electron pair of the methyl group adjoining an unsaturated carbon atom remained less localized than the electron pair of the adjacent C-C bond and this apparently gave rise to the increased capacity of methyl to donate (free or repel) the electrons of the C-H bond by the mechanism:



or expressed differently to show the "completed" process of electron donation:



According to its authors, the Baker-Nathan effect includes, naturally, ethylene systems. Furthermore, Baker and Nathan also considered that this same process of electron donation from methyl would be observed in systems with one single bond in which the X-group could exist as an anion.*

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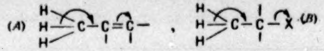
* It should be noted that in the terminology of the English school, the Baker-Nathan effect appeared as a hypothetical tautomeric + T -effect [2].

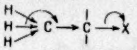


At approximately the same time, Wheland [3] developed fundamentally identical ideas and somewhat later was followed by Mulliken et al. [4] and in the terminology of the American school the above reaction of single and double bonds was called hyperconjugation of the first order and the reaction of single bonds – hyperconjugation of the second order.

Together with the static and dynamic induction and tautomeric effects of the English school, the Baker-Nathan effect was included by the authors of the theory of double reaction capacity and transfer of reaction center, in the basis of the theory. They accepted this effect (like other effects) including the concrete interpretation of the corresponding electron mechanism by the English school [5,6], renamed it (as all other effects of the English school) in conformity with the reacting bonds as $\sigma\pi$ -conjugation and $\sigma\sigma$ -conjugation and explained the motives for the renaming [8]. Furthermore, they somewhat enlarged the Baker-Nathan effect, including in it the conjugation of single bonds with single nonacceptors; it was considered not only static (T_s) but also dynamic (T_d) [9,7]. The Baker-Nathan effect ($\sigma\pi$-, $\sigma\sigma$-conjugation) as is known, has been used by workers in this field of theoretical chemistry as the basis for explaining a wide range of reactions [10], among them β-elimination etc. [11,12].

II. Members of the English school stressed the fact that these effects formulated by them, including the Baker-Nathan effect, are not direct findings nor observations of actually existing electronic processes in a molecule. These effects were not directly established nor observed facts of electronic mechanisms in a molecule, but only hypotheses on them; postulations put forward to explain various experimental facts of the reaction capacities of different materials [13]. With such a hypothetical character these effects of the English school cannot be detected by direct chemical investigation of the reaction, as the authors themselves and the proponents of this trend have realized and noted in numerous statements [14-16]. It is not surprising that which such a situation the hypothetical effects appear not as clearly defined laws derived from nature, but more often as ad hoc explanations [17]. Naturally, the problem of direct experimental testing of the hypotheses of the English school, which have remained only hypothetical up to the present, presents great interest in many respects. In this work we considered only the Baker-Nathan effect from this point of view and briefly, in passing, the inductions (± I) as well.

III. The possibility of testing these effects by direct experiment results from the following considerations on the electronic mechanism. It is customary in the English school [18] to differentiate between donor and acceptor bonds in molecules with the supposed hyperconjugation mechanism of electron displacement put forward by Mulliken [4]. The donors give (repel, free) electrons, the acceptors take them. In molecules of the (A) and (B) type (see above) the C-H bonds of methyl groups, $C = C$ and C–X bonds are donors and C-C bonds are acceptors. We note that with appropriate molecular structure the supposed inductive effect + I (expressed →) increases the electromeric Baker-Nathan effect (+ T). It can also be augmented by the supposed induction effect (–I) (effect of attracting electrons, for example, by the halogen of the molecule; this is also expressed by a straight arrow →) [19]. Thus, in a molecule of appropriate structure (when X = halide), all three effects (+ T, + I, –I) may be hypothetically superimposed and in that case strengthen each other [20]:



By the very nature of the electronic mechanism described, the interatomic distance of donor bonds should increase and the bond energy should decrease. In particular, hydrogen atoms in the methyl group should ionize to a greater or lesser extent, namely – protonize; the donor double bonds should lose some of their double bond character and the triple, their triple bond character. The acceptor C-C bonds, on the contrary, become to a certain degree, double bonded, and should strengthen and contract. The authors themselves point out the consequences of these effects [4, 21, 22].

However, the lengthening or contracting of bonds and the decrease or increase of their energy may be, in the main, tested by direct experiment. As according to the hypothesis, this is due to the electronic mechanism of the effect studied, then it would be possible to check directly by experiment the hypothesis on the electronic mechanism of the Baker-Nathan effect.

IV. In their monographs [23,24], Baker and Ingold turned to this proof (using data on the interatomic distances) and attempted to observe hyperconjugational lengthening of donor bonds and hyperconjugational contraction of acceptor bonds (the measurement of energy from this point of view is more difficult). However, they did not find definite confirmation of hyperconjugation in this data and they put forward the proposition that the hyperconjugational displacements in the interatomic distances are probably minute and that they cannot be measured as present day methods are not sufficiently accurate [23,28].*

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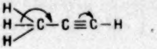
* In this connection special importance is attached to the single case noted by Ingold of a possible spectroscopic observation which showed lengthening of the C-H donor bond of the methylacetylene methyl group, as a result of hyperconjugation of the first order ($\sigma\pi$ -conjugation):



This case is the more important as it concerns the methyl group which has a deciding role, that of initiator, in the Baker-Nathan effect. Therefore, it undoubtedly requires a thoroughly detailed consideration.

On the subject of this delicate experiment, Ingold wrote [28]: "The spectroscopic method was most suitable for measuring insignificant change in interatomic distances and by using it exact bond length measurements were made on the C—H of the methylacetylene methyl group, which showed its slight lengthening," namely – by 0.003A (see Table below). However, there is in fact no accurate experimental data of this kind of hyperconjugational lengthening of the C-H bond of the methylacetylene methyl group. In establishing this lengthening Ingold appeared (at best) to be simply confused in citing the pertinent data. Actually, he presents [29] in his Table the following data on the C-H bond of the methylacetylene methyl group (in A):

Compound	Bond	Calculated from atomic radii	Found	Method	Reference
$CH_3-C\equiv C-H$	$H-CH_2-$	1.094	1.097	spectroscopic	[3]

R. Trambarulo, W. Gordy, J. Chem. Phys., 18, 1613 (1950). Instead of the calculated C—H distance, the observed value is shown for methane.

However, in the paper by Trambarula and Gordy, cited by Ingold, the following data was given on the literatomic distances of methylacetylene (in A) [30]:

Compound	C—H methyl	C—C	C≡C	C—H acetylenic
$CH_3-C\equiv CH$	1.097± 0.010	1.460 ± 0.002	1.207 ± 0.002	1.056 ± 0.008

The radiospectroscopic data given by Trambarulo and Gordy, like the spectroscopic data, must also involve calculations. Although, Ingold took the figure 1.097 without indicating the limits of experimental error in the work of these authors, the latter determined it with an accuracy of ± 0.010 A. Ingold, however, talks of accurate

V. There is, however, one intrinsic molecular parameter, as it is a dynamic system, whose measurement makes it possible to test the electronic mechanism of the Baker-Nathan effect in the above sense even with the present state of spectrographic techniques. This parameter is the frequency of molecular oscillation.

As is known, a completely determined relation exists between the direction of change in the energy of a bond, its interatomic distance and characteristic oscillation frequencies: this relation is that an increase in bond energy is always accompanied by a contraction of its interatomic distance and an increase in its oscillation frequencies, and, on the other hand, a decrease in bond energy is always accompanied by an increase of its interatomic distance and a decrease in its oscillation frequency [32].

This may be illustrated by the data in the table on carbon-carbon, carbon-oxygen and carbon-hydrogen bonds [33].

As can be seen from the Table, the range of variation of oscillation frequencies of the bonds is much greater than the range of variation of their interatomic distances:

		Increase in oscillation frequencies	Contraction of interatomic distances
Percentage variation during transition from	C–C to C≡C	+100	−23
	C–O to C≡O	+ 108	−20
	CH to CH acetylene	+20*	− 5

By this method, using the changes in their oscillation frequencies (in the case of maximum conservation, of course, of their characteristic) it is possible to decide on the directions of changes in interatomic distance of various bonds, which, due to their small value, are difficult to detect directly. We used this for direct experimental solution of the problem – whether or not the hypothetical electronic mechanism of the Baker-Nathan effect corresponded to reality; in this work we limit ourselves to a problem whose clarification is of greatest importance for the mechanism of this effect: is it a fact in those molecules in which the Baker-Nathan effect is supposed to occur, that the methyl group donates (frees, repels) electrons (thus inducing the effect) which, as noted above, due to the very nature of such an electronic mechanism must necessarily result in an elongation of the C-H bonds of the methyl group, in a decrease in their energy and in a corresponding lowering of their oscillation frequencies; the observation of an opposite phenomenon would be an absolute refutation of the hyperconjugation electronic mechanism.

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measurement of hyperconjugational lengthening of the C-H bond of the methylacetylene methyl group by 0.003 A, which lies within the limits of error given by Trambarulo and Gordy for their expriment (0.010 A).

However, as can be seen from the notes to the Table (see above) Ingold did not take the value of the C-H bond length, 1.097 A, from the radiospectroscopic work of Trambarulo and Gordy, but termed this value as being "calculated" and substituted it without disclosing its source, as though it had been observed spectroscopically for methane (although spectroscopic, as well as radiospectroscopic, determination of interatomic distances involve appropriate calculations). However, up to the present time, the value of the C-H bond length in methane spectroscopically determined by Gertsberg is the one usually referred to [31]. Gertsberg determined it as being equal to 1.0936 A, which is less rather than more than the "normal" value of 1.094 A.

But probably, the greatest misunderstanding arises from the fact that there can be no talk of hyperconjugation at all in methane and especially of hyperconjugation of the first order. Therefore, the substitution of the C-H bond length of methane for that of the C-H bond in the methylacetylene methyl group, to determine the hyperconjugational effect in the latter in this way and the description of the hyperconjugational stretching of the C-H bond thus formed as the only very accurate experimental discovery of this lengthening, are assertions which require, of course, no further consideration.

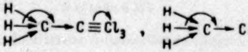
Finally it appears from all this that Baker and Ingold did not succeed in confirming directly by experimental data on interatomic distances, the electronic mechanism of the Baker-Nathan effect, i.e. hyperconjugation of the first order ($\sigma\pi$ -conjugation); they did not even mention the verification of hyperconjugation of the second order ($\sigma\sigma$ -conjugation).

* Increase from 2824 to 3372 cm^{-1}.

VI. As is known from optical investigation of normal paraffins, the frequencies of the C-H bonds of the methylene and methyl groups (lying within extremely characteristic frequency ranges) are independent of one another in the sense that on the addition of methylene groups with the elongation of the carbon chain, their frequencies remain practically unchanged, and similiarly for methyl groups, and only their intensity changes. The intensity of the methylene group frequencies increases and the intensity of the methyl group frequencies relatively decreases as the number of the latter does not increase. The following are frequencies of methyl and methylene groups of normal paraffins [34]:

CH_2	2853	—	2908	—	—
CH_3	—	2879	—	2938	2967

If, for example, some strongly electronegative atom is introduced into the molecule, the frequencies of these groups may be displaced strongly under its effect; furthermore, due to their independence, the frequencies, for example, of adjacent methylene groups could increase greatly while the frequencies of remote methyl groups could remain without change and so on. We refer to such molecules as:



The Baker-Nathan effect should, supposedly be increased in them by the effects + I and − I. The hypothetical operation of these effects, should result in sharp protonization of the hydrogen atoms of the methyl group C-H bonds and as a direct result of this, in the increase of the C-H bond interatomic distances, and in decrease of their energy and the lowering of the oscillation frequencies. Actually, nothing of the kind happens in these molecules, and on the contrary, in comparison with those of similar normal paraffins, the oscillation frequencies of those C-H bonds sharply increases, which indicates a decrease in their bond energy. The above is clearly illustrated by a comparison of the methyl C-H bond oscillation frequencies for these molecules and ethane (cm^{-1}) [33a].

Oscillation Frequencies, Bond Energies and Interatomic Distances in Single and Multiple Bonds

Bonds	Compounds	Oscillation frequency (cm^{-1})	Bond energy (kcal/mol)	Interatomic distance A
I. Carbon-carbon				
C−C	C_2H_6	992	68	1.550
C=C	C_2H_4	1621	78	1.353
C≡C	C_2H_2	1974	114	1.203
II. Carbon-oxygen				
C−C	CH_3OH	1033	86.5	1.43
C=O	CH_3CHO	1720	134	1.22
C≡O*	CO	2155	211	1.128
III. Carbon-hydrogen in single and multiple bonds				
radical	CH	2824	80.0	1.120
with ordinary bond**	C_2H_6	2730—2960	88.4	1.098
with double bond**	C_2H_4	2988—3107	106.0	1.076
with triple bond	C_2H_2	3228, 3372	121.0	1.060

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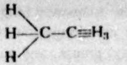
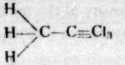
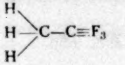
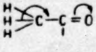
* Langmuir, Gertsberg and other authors write of the almost triple bond of carbon monoxide; it is symbolized as C ≡ O to differentiate it from the preceding ones.

** The limits of the frequency range of the C-H bond are indicated.

	2880	2940	2960	—	—
	—	2938	—	3002	—
	—	—	2974	—	3040

There is also no hypothetical Baker-Nathan effect in acetaldehyde, which was supposed to have hyperconjugation of the first order  , on the contrary, the frequencies of the methyl group (as those of methine) are greatly increased, that is the interatomic distances of these bonds contract, while their energies are increased:

Frequencies of paraffin C-H bonds [34]:

Methyl group	—	2879	—	2938	2967	—
Methine "	2870	—	—	—	—	—

Frequencies of H_3CCHO:

Methyl group	—	—	2917	—	2967	3015
Methine "	—	—	—	—	2967	—

The data presented show as well that particularly where C-H bonds are concerned, there is no justification for the hyperconjugation electronic mechanism and mechanism of the −I effect, nor is there any for the electronic mechanism of the electrostatic effect +I in the simplified version of the English school, which typically extends it to all bonds without considering their specific cases. Actually, under the effect of an adjacent halide or of another strongly electronegative atom, C-H bonds do not protonize (as for example O-H bonds [32], in chloroacetic acids) that is, there is no increase of interatomic distance or decrease of bond energy and oscillation frequencies; on the contrary, they electronize sharply in the sense that their interatomic distance contracts, the bond energy increases and the oscillation frequencies rise. This electronization of C-H bonds under the effect of halides is well illustrated by data on the considerable increase in their frequencies in symmetrically substituted chloroderivatives of ethane and other compounds (cm^{-1}).

Paraffins [34]:						
CH_2	2853	—	2908	—	—	—
CH	—	2870	—	—	—	—
$ClCH_2—CH_2Cl$:						
CH_2	—	—	—	2956	—	3002
$Cl_3Si—CH_2Cl$:						
CH_2	—	—	—	2935	2987	—
$Cl_2CH—CHCl_2$:						
CH	—	—	—	—	2984	—
$Cl_3Si—CHCl_2$:						
CH	—	—	—	—	2963	—

In electronuclear reactions, the C-H bond in a molecule behaves very differently from the O-H bond, but this, however, will not be discussed in the present article.

As we saw, Baker and Ingold supposed that the Baker-Nathan effect would be specially strong in the acetylenic compounds, in particular, in methylacetylene, and as a result the C-H donor bonds of the methyl group should be elongated in them. Actually, the frequencies of C-H bonds of the methylacetylene methyl group are sharply increased and there can be no hyperconjugational lengthening (cm^{-1}):

Frequencies of the methyl group C-H					
	normal paraffins	2879	2938	2967	–
	$CH_3-C\equiv CH$	–	2927	–	2979

As the data presented show, electronuclear reactions in molecules are incomparably more complicated than is supposed in the hypothetical effects of the English school, in particular the Baker-Nathan effect, the latter being in no way confirmed by the direct experimental data presented, which lies well beyond the limits of experimental error; on the contrary, the electronic mechanism proposed is refuted by this data.

SUMMARY

Optical data on the characteristic oscillation frequencies of molecules permit direct experimental testing of the accuracy with which the Baker-Nathan effect conforms to reality. This data, which lies well beyond the limits of experimental error, very definitely shows that the electronic mechanism, admissible by the Baker-Nathan hypothesis, is not only not confirmed experimentally, but, on the contrary, refuted. All this indicates that electronuclear reactions in a molecule are more complex than is supposed by the Baker-Nathan hypothesis.

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see [2,3,5 d].

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[9] See [5a], p. 14; see also [2b], p. 192 et seq.; [4].

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[21] See [2a], p. 43.

[22] See [7a], p. 148.

[23] See [7b], p. 19 *et seq.*

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Institute of Mineral Fuels Academy of
Sciences USSR

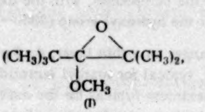
INVESTIGATION IN THE FIELD OF CYCLIC ACETALS OF HYDROXYCARBONYL COMPOUNDS

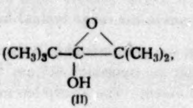
VII. PREPARATION AND PROPERTIES OF EPOXYOCTENOL METHYL LACTOLIDE

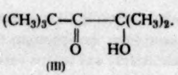
(α-METHOXY-α-TERT-BUTYL-β,β-DIMETHYLETHYLENE OXIDE)

T. I. Temnikova and S. S. Skorokhodov

The preparation of epoxyoctenol methyl lactolide (I), described for the first time in the present work, was interesting from two points of view. On the one hand, methyl lactolides of α-keto alcohols of the aliphatic series were unknown up to the present time, and the material (I) prepared by us is the first example of such a compound. On the other hand, it is a derivative of epoxyoctenol, a material that had already been prepared by A. M. Butlerov [1] and to which a α-hydroxy oxide structure (II) had been ascribed for a long time. It is established at the present time that epoxyoctenol is a keto alcohol (III).


(I)


(II)


(III)

The structure of epoxyoctenol was proved by T. I. Temnikova and M. P. Tikhomolova [2] in 1951 using a spectrochemical method. The conclusion that epoxyoctenol has a structure corresponding to formula (III) was based on chemical data [1,3] and on the presence in the ultraviolet spectrum of typical C=O group absorption in the range 280-300 mμ (λ_{max} 295 mμ), as well as of combination light scattering frequencies (1689 cm^{-1}) also typical for the same group. In 1955, the combination light scattering spectrum of epoxyoctenol was redetermined by Batuev and Antsus but over a wider frequency range [4] and they confirmed the conclusion drawn in the work above that epoxyoctenol had a hydroxy ketone structure while on the basis of a broadened line at 3522 cm^{-1} they concluded that there was a hydrogen bond between the C=O and OH groups.* The formation of a hydrogen bond results in additional stabilization of the α-keto alcohol structure relative to that of the α-hydroxy oxide one, pseudomeric with it; if the latter exists in equilibrium with the α-keto alcohol it must be in a vanishingly small amount [2]. Although the α-hydroxy oxide forms are incapable of independent existence as was established in a series of papers of which this is the most recent, their methyl derivatives– methyl lactolides– are completely stable [5]. It therefore seemed likely, theoretically, that in the case of epoxyoctenol the hydroxy oxide form could also be fixed as a methyl lactolide, and this is proved in the present paper.

Epoxyoctenol methyl lactolide was obtained by the usual method – by the action of sodium methylate on bromopentamethylacetone. Absolute ether or dry methyl alcohol was used as the reaction medium. The latter was more convenient in this case as the reaction then took place in a homogenous medium. Usually methyl lactolides react on boiling with alcohols [5]. In this case, however, the reaction of the methyl lactolides being formed with methyl alcohol was inhibited by the steric hinderance of the tert-butyl group which obstructed the approach of the methyl alcohol molecule to the carbon atom, adjacent to the methoxyl group, which due to its overwhelming reactivity was the reaction center. Besides epoxyoctenol methyl lactolide, an insignificant amount of a material was obtained with a somewhat higher boiling point, which contained, to judge from the spectrochemical data, a large amount of methoxypentamethylacetone. The reaction was considerably slower when carried out in absolute ether and an insignificant amount of the higher boiling material was likewise formed. Due to the fact that oxidation could have taken place during the sodium methylate treatment of bromopentamethylacetone and that the higher fraction could have contained the methyl ester of the acid, part of this fraction was heated for a long time (100 hours) with aqueous alkali at 100°. No salt of the organic acid was found in the aqueous alkaline layer.

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* We consider it necessary to note that M. I. Batuev and L. I. Antsus [4] do not give a new formula for epoxyoctenol but only present refinements of the hydroxy ketone one. We cannot agree with their statement that the keto alcohol formula is inconsistent with chemical experiment [see 1-3]. The inertness of epoxyoctenol towards substituted hydrazines is explained by the inaccessibility of the carbon atom of the C=O group, for the same reason that pentamethylacetone does not react with phenylhydrazine, semicarbazide and other similar reagents. However, the conversion of epoxyoctenol into methyl-tert-butylacetylcarbinol; by H^+ under relatively drastic conditions [6], doubtlessly is accomplished in a complex with a proton, in the cation, with the formation of an hydroxy oxide type of structure [7].

The hydrolysis of epoxyoctenol methyl lactolide was very easily achieved by shaking it with dilute acid in the cold and gave pure epoxyoctenol. An attempt to isomerize epoxyoctenol methyl lactolide into the methyl ether of the isomeric keto alcohol – methyl-tert-butylacetylcarbinol– was unsuccessful. Isomerization did not take place when it was heated with $ZnCl_2$ at 130-140° for 1 hour 30 minutes [8]; the material, separated in the usual manner, remained unchanged.

In previous work we have recorded infra-red absorption spectra of aliphatic-aromatic α-keto alcohol methyl lactolides and of substances genetically related to them – ketones, keto alcohols and isomeric keto alcohol methyl ethers; from them it was established that the frequency 917 cm^{-1} was typical for the oxide ring of the aliphatic-aromatic α-keto alcohol methyl lactolides.

In the present work we determined the infrared absorption spectra of pentamethylacetone, epoxyoctenol, its methyl lactolide and fractions that distilled somewhat higher than methyl lactolide and which apparently, contained mainly methoxypentamethylacetone. The measurements carried out were on an infra-red spectrometer type IKS-6 in the ranges 770 – 970 cm^{-1} (12.9 – 10.3 μ), 1550– 1800 cm^{-1} (6.5 – 5.5 μ) (NaCl prism) and in the range 3350– 3650 cm^{-1} (2.98– 2.75 μ) (LiF prism). None of the compounds, with the exception of epoxyoctenol, had an absorption maximum in the range typical for the hydroxyl group (3350– 3650 cm^{-1}).

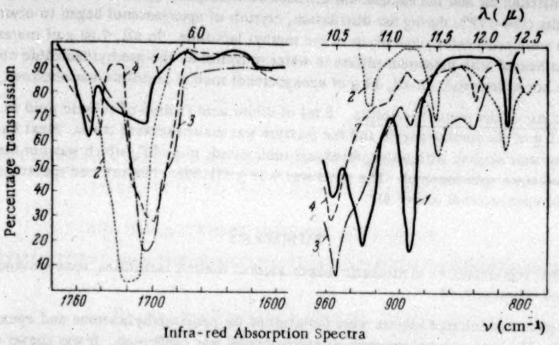
The methyl lactolide (I) spectrum was determined in both ranges on a thin layer, $d = 3\,\mu$ (figure , curve 1). It can be seen from the spectrum that the frequency 917 cm^{-1}, typical for methyl lactolides of the aliphatic-aromatic series, was in this case absent. The absorption maximum typical for the oxide ring in the range 770-970 cm^{-1} was at 893 cm^{-1} (11.20 μ). For comparison we determined spectra of two aliphatic oxides: unsym. methylethylethylene oxide had a maximum at 903 cm^{-1} (11.07 μ) and hexene-1 oxide had a maximum at 898 cm^{-1} (11.13 μ). It should be noted that methyl lactolides of the aliphatic-aromatic series also had a maximum at ~ 900 cm^{-1}, but it was less characteristic [8]. There was some decrease in transmission in the carbonyl range near 1710 cm^{-1} due to insignificant traces of methoxyketone.

The spectrum of pentamethylacetone was determined on the range 770-970 cm^{-1}, on a thin layer, $d = 30\mu$; at 890 cm^{-1} there was no substantial decrease in percentage transmission; in the carbonyl range 1550-1800 cm^{-1} it was determined in a carbon tetrachloride solution, $c = 2.52\%$, $d = 270\mu$. The maximum was at 1724 cm^{-1}.

The spectrum of the fraction, with a boiling point somewhat higher than methyl lactolide, was determined in the range 770-970 cm^{-1} on a thin layer, $d = 30\mu$. A small maximum at 893 cm^{-1} was explained by methoxyoxide traces. In the carbonyl range, the spectrum was determined in CCl_4, $c = 1.64\%$, $d = 270\,\mu$. The absorption maximum was at 1706 cm^{-1}.

The spectrum of epoxyoctenol (III) was determined in the range 770-970 cm^{-1} as a suspension in vaseline oil (20 mg of material per 3 drops of oil, $d = 100\mu$). Transmission did not decrease near 890 cm^{-1}. In the carbonyl range it was determined in a CCl_4 solution, $c = 1.74\%$, $d = 270\,\mu$. The absorption maximum was at 1700 cm^{-1}.

In conclusion it is interesting to compare briefly in relation to their stability the properties of the methyl lactolides prepared with those known for keto alcohol methyl lactolides. Up to the present time 15 methoxyoxides have been described, 12 of them contained aromatic nuclei in the oxide ring. At the end of 1954 Stevens et al. obtained the first two samples of aliphatic α-hydroxyaldehyde methyl lactolides [9]. In



Infra-red Absorption Spectra

1) Epoxyoctenol methyl lactolide; 2) pentamethylacetone; 3) fraction with a somewhat higher boiling point than methyl lactolide; 4) epoxyoctenol.

comparison with the latter the substance prepared by us differed in an exceptionally great stability, as it was completely distilled without change at normal pressure and could also remain unchanged for a long time (2 years). While on the contrary the methyl lactolides of aliphatic hydroxyaldehydes obtained by Stevens et al. were easily changed by boiling. The methoxyoxide obtained by us was also, in this respect, considerably more stable than methyl lactolides of secondary aliphatic-aromatic α-keto alcohols.

EXPERIMENTAL

Preparation of Dimethyl- trimethylacetyl-carbinol (Epoxyoctenol) (I).

1. Preparation of bromopentamethylacetone. Pentamethylacetone was prepared by I. N. Nazarov's method [10]. A. P. Terentev and L. A. Yanovskaya's method [11] was used for its bromination. 20.53 g of ketone was dissolved in 20 ml of dioxane and 45 g of dioxane dibromide was added to the solution in small portions. The reaction went slowly and was completed by heating to 70-80° for 1.5 hours. On cooling, the reaction mass was poured into water and the oil was extracted with ether. The ether extract was washed with water and dried over $MgSO_4$. 27.3 g of bromoketone was obtained with b.p. 52-53° at 7 mm, yield 82.7%. According to [12] the b.p. is 62-64° at 12 mm.

2. Preparation of methyl lactolide (I). 5.7 g of sodium was dissolved in 220 ml of dry methyl alcohol. While this was cooled in ice water, 42.29 g of bromopentamethylacetone was added over a period of 1 hour. Mixing was continued at room temperature for 4 days. The completion of reaction was determined by the Beilstein test. Then carbon dioxide, which had been washed with water and dried with sulfuric acid and calcium chloride, was passed through the solution. When precipitation was complete, the precipitate was filtered off very rapidly (in 2 - 3 minutes).

a) Treatment of the filtrate. The filtrate was at once transfered to a distillation flask, the methyl alcohol was distilled off at atmospheric pressure and then the methyl alcohol distilled off and the residue were fractionated on a column. A material was obtained with b.p. 77-78° at 74 mm and 154-155° at normal pressure. The methyl lactolide had a strong camphor smell, was very volatile, despite the relatively high boiling point and did not resinify or polymerize on distillation. The infrared spectrum did not have absorption maxima characteristic of OH and C=O groups, but, in the region characteristic of oxide rings, it had a maximum at 896 cm^{-1} (figure , curve 1).

d_4^{20} 0.8916, n_D^{20} 1.4173, MR_D 44.65 calc. 44.98.
Found %: C 67.91, 68.01; H 11.46, 11.32. OCH_3 20.0. $C_9H_{18}O_2$. Calculated %: C 68.31; H 11.47; OCH_3 19.6.

Besides the initial fraction from the distillation, a small fraction (2 g) was isolated, with b.p. 70-71° at 37 mm, n_D^{20} 1.4260, which, from spectral data and its stability to hydrolysis, appeared to be methoxypentamethylacetone (curve 3).

b) Treatment of the precipitate. The precipitate, which was saturated with a liquid material, was dissolved in water; the organic material was extracted with ether and the ether extract was dried with Na_2SO_4. The ether was distilled off and the residue was distilled at atmospheric pressure. The material distilled between wide limits (154-172°); during the distillation, crystals of epoxyoctenol began to crystallize out in the receiver, which were produced by hydrolysis of the methyl lactolide. In all, 7.33 g of material was obtained. The product was heated with potassium sulfate in water to hydrolyze the methyl lactolide completely. 0.95 g of material was not hydrolyzed. In all, 17 g of epoxyoctenol methyl lactolide was obtained, representing 53%.

3) Hydrolysis of the methyl lactolide. 2 ml of dilute acid (1 drop of sulfuric acid in 50 ml of water) was added to 0.2 g of the methoxyoxide and the mixture was shaken several times. Next day white crystals came out. They were washed with water, dried and sublimated; m.p. 49°, which was not depressed by admixture with authentic epoxyoctenol. The yield was 0.13 g (71.3%). The infrared spectrum corresponded to that of authentic epoxyoctenol (curve 4).

SUMMARY

1. The first representative of aliphatic α-keto alcohol methyl lactolides, epoxyoctenol methyl lactolide, was prepared and characterized.

2. Absorption and infrared spectra were determined for pentamethylacetone and epoxyoctenol and its methyl lactolide. The keto alcohol structure of epoxyoctenol was confirmed. It was shown that the characteristic frequency for the oxide ring of epoxyoctenol methyl lactolide was 897 cm^{-1}.

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Leningrad State University

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INVESTIGATION OF THE REACTION OF PINACOLS CONTAINING SUBSTITUTED ACETYLENE RESIDUES

XII. THE ACTION OF MERCURIC ACETATE ON UNSYMMETRICAL DIMETHYLPHENYLPHENYLACETYLENYL-ETHYLENEGLYCOL

E. D. Venus-Danilova and A. Fabritsy

In a previous report [1] we described the reaction of unsymm. dimethylphenylphenylacetylenyl-ethyleneglycol with mercuric chloride and bromide. It was shown that the action of mercuric chloride on this glycol produced, in addition to the complex salt 5,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuran-2,5, the isomerization of the glycol into the 2-hydroxydihydrofuran-2,5, and also an organomercuric compound, which however, could not be isolated, but whose presence was proved by the formation of its symmetrization product on treating the organomercuric compound with ammonia gas.

A scheme for the reactions of unsymm. dimethylphenylphenylacetylenyl-ethyleneglycol was proposed.

In this report we give the results of the action of mercuric acetate on the same glycol. We selected mercuric acetate in the hope that with this strong mercurating agent it would be possible to isolate the organomercuric compounds thus formed and to investigate them more closely.

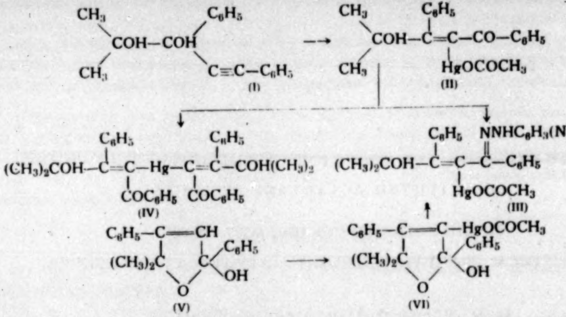
Actually, in this case the reaction of unsymm. dimethylphenylphenylacetylenyl-ethyleneglycol with mercuric acetate in an alcohol medium did form an organomercuric compound which was successfully isolated and some of whose derivatives were prepared.

The dimethylphenylphenylacetylenyl-ethyleneglycol (I) reaction with mercuric acetate was carried out in acetic acid and alcohol media. Probably, the organomercuric material (II) (2-methyl-3,5-diphenyl-4-acetomercuripenten-3-ol-2-one-5), was produced in acetic acid and this material corresponded to the mercurated, ethylene γ-keto alcohol (2-methyl-3,5-diphenylpenten-3-ol-2-one-5) (diagram) and possibly a trace of the hydroxydihydrofuran was produced whose formation can be explained in this case by effect of the acidic medium. The mercurated γ-keto alcohol could not be isolated from the mixture of reaction products in acetic acid, as a thick sticky mass was formed which hardened very rapidly into a glasslike product.

A crystalline substance (II) could be isolated from mercuric acetate by treatment of the glycol in alcohol solution. The crystalline and glasslike products formed the same 2,4-dinitrophenylhydrazone, (III) containing mercury, and according to analysis data, corresponding to the 2,4-dinitrophenylhydrazone of a mercurated ethylene γ-keto alcohol (II).

The action of calcium chloride on the glasslike (from the acetic acid solution) and the crystalline (from the alcohol solution) organomercuric compound resulted, not in replacement of the acetic acid residue by halogen, but by a systematization reaction [2] with the formation of the same material. In contrast to the cyclic systematization product, obtained by ammonia treatment of the organomercuric compound from the glycol and mercuric chloride [1], an open structure can be ascribed to this substance (IV) [4-di-(2-methyl-3,5-diphenylpenten-3-ol-2-one-5)-mercury].

The glycol reactions with mercuric acetate are analogous to reactions with mercuric chloride and are shown in the scheme.



In this case, in contrast to mercuric chloride reaction with the glycol, cyclization of the organomercuric compound (II) into the mercurated 2-hydroxydihydrofuran (VI) (5,5-dimethyl-2,4-diphenyl-3-acetomercuri-2-hydroxydihydrofuran-2,5) did not take place; therefore an open form may be ascribed to the symmetrization product of this organomercuric compound (IV).

The organomercuric compound (II) was decomposed by hydrochloric acid and a mercuric complex was immediately precipitated, [3].

5,5-Dimethyl-2,4-diphenyl-2-hydroxydihydrofuran-2,5 (V) was mercurated by mercuric acetate for comparison with the organomercuric compound (II) obtained from the glycol. It was found that mercuric acetate, being a strong mercurating agent, mercurated 2-hydroxydihydrofuran-2,5 with the formation of a substance (VI), different from the organomercuric compound (II). The mercurated hydroxydihydrofuran on symmetrization by calcium chloride, was converted into the cyclic symmetrization product, obtained by ammonia treatment of the reaction product from the glycol and mercuric chloride (1).

Mercurated hydroxydihydrofuran (VI) also gave the same 2,4-dinitrophenylhydrazone as the product obtained by mercuric acetate treatment of the glycol, as during the formation of mercurated hydroxydihydrofuran 2,4-dinitrophenylhydrazone the substance (VI), like hydroxydihydrofuran, reacted in the open form corresponding to an ethylene γ-keto alcohol.

It should be noted that the organomercuric compounds, formed by mercuric acetate treatment of the glycol and hydroxydihydrofuran could not be obtained in a sufficiently pure state, as their analyses showed. These substances were very soluble in all usual organic solvents and separated from the solutions as an oily mass, while, on the contrary, their symmetrization products were characterized by very low solubility.

EXPERIMENTAL

Experiment 1. Mercuric acetate and the glycol in acetic acid solution. 5 experiments were carried out in 60% acetic acid, in which the ratios of glycol to mercuric acetate were 1:1, 1:2 and 1:0.33. In all the experiments and temperature was about 80° and heating was continued for 2½ to 4 hours.

On mixing the acetic acid solutions of the glycol and the mercury salt slight heat was evolved and a very small white precipitate appeared. After cooling, the reaction mixture was diluted with water and the emulsion produced was either immediately extracted with benzene or before extraction was neutralized with bicarbonate. In all the experiments, a thick, yellowish, uncrystallizable mass was obtained, which thickened very much on standing and was converted into a transparent glasslike mass, which was readily soluble in ether and benzene and more difficultly in alcohol and gasoline. The material quickly decolorized potassium permanganate and gave positive reactions for hydroxyl (methylmagnesium iodide) and carbonyl (2,4-dinitrophenylhydrazine) groups.

Analysis of the glasslike material and the thick, viscous mass, obtained immediately after distilling off the benzene, did not give satisfactory results corresponding to the production, by treatment of the glycol with mercuric acetate, of material (II) (2-methyl-3,5-diphenyl-4-acetomercuripenten-3-ol-2-one-5), which corresponds to mercuration of the γ-keto alcohol $C_{20}H_{20}O_4Hg$ (C 45.75; H 3.81; Hg 38.24; OH 3.24; M 524.6).

The analysis data on the glasslike material, obtained in different experiments, gave high carbon (55.89, 56.34%) and hydrogen (4.59, 5.62%) contents and low mercury content (24.01, 26.79, 25.70%), which indicated that the material contained an admixture of either original glycol or what was more probable, the hydroxydihydrofuran (81.20% C and 6.77% H).

Determination of the mol. weight gave sufficiently satisfactory results (531, 575) and also the determination of the number of hydroxyl groups (1.02 and 1.01 or 3.30 and 3.27%).

Yields of glasslike material varied from 83.5 to 97%, for a ratio of 1 mole of glycol; 1 mole $(CH_3COO)_2Hg$ up to 51% for a ratio of 1:0.33.

The dinitrophenylhydrazone of the glasslike material came out at once as an orange-yellow precipitate under the usual conditions [4]. After 2 hours the precipitate was filtered off and washed with a small amount of alcohol and then with ether. Recrystallization of the precipitate did not succeed as this made it darker and stickier. On determining the melting point of the washed 2,4-dinitrophenylhydrazone containing mercury, it began to change at 100° and decomposed at 144-145° (III).

Found %: N 7.98, 8.19; Hg 28.86. $C_{16}H_{24}O_7N_4Hg$. Calculated %: N 7.99; Hg 28.46.

Action of sulfuric acid on the glasslike material. The material dissolved in strong sulfuric acid in the cold without forming a tar; slight fluorescence appeared at the beginning. On diluting the solution, it became slightly turbid and a distinct violet-green fluorescence appeared.

20% sulfuric acid easily dissolved the material with slight warming and fluorescence appeared. After precipitation of ionic mercury from the solution with hydrogen sulfide, separation of the mercuric sulfide, neutralization of the solution and extraction with ether, we isolated 2-hydroxydihydrofuran-2,5 with m.p. 99-100°.

Action of hydrogen chloride on the glasslike material. Passing hydrogen chloride through the ether solution separated out the yellow mercury complex [3] of 5,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuran-2,5 with m.p. 160-161° (with decomp.).

Decomposition of the glasslike material with hydrochloric acid was carried out by adding 3 ml of concentrated hydrochloric acid to a solution of 3 g of glasslike material (with 26.79% Hg) in 25 ml of ethyl alcohol. The solution began to turn yellow and became turbid at room temperature. After heating, the yellow precipitate which came out was filtered off and washed with alcohol, benzene and ether. 2.3 g of a crystalline yellow complex with m.p. 160-161° (with decomp.) was isolated. On adding two drops of concentrated hydrochloric acid to the filtrate and heating, no further precipitate separated. The alcohol was distilled off from the filtrate, water was added to the residue and the solution was neutralized with bicarbonate and was extracted with benzene. After distilling off the benzene, a thick mass remained, which crystallized and was found to be 2-hydroxydihydrofuran-2,5.

Analysis of precipitated complex with m.p. 160-161° (decomp.).
Found %: Hg 35.05; Cl 17.99. $C_{18}H_{17}OHgCl_3 \cdot H_2O$. Calculated %: Hg 34.96; Cl 18.55.

From the percentage of mercury in the original glasslike material (26.79%) it follows that the 3 g of material taken contained 0.804 g of mercury; as 2.3 g of complex, containing 34.96% of mercury, (which corresponded to 0.804 g of mercury) was obtained from that amount of glasslike material, practically all the glasslike material was converted into the mercury complex.

Action of calcium chloride in methyl alcohol on the glasslike material. On mixing an alcohol solution of the glasslike material with an alcohol solution of calcium chloride [2], fine colorless crystals began to separate. After 15 hours the crystals were filtered off, washed with alcohol, water and again with alcohol and dried in air. The m.p. was 154-155°. Recrystalization did not succeed as the material was insoluble in alcohol and ligroin and its solubility in benzene did not change on raising the temperature.

The material reacted with methylmagnesium iodide, but quite slowly; it contained mercury, gave a negative reaction for chlorine and gave a violet fluorescence with sulfuric acid, like 2-hydroxydihydrofuran-2,5. The structure of the material probably corresponded to 4-di-(2-methyl-3,5-diphenylpenten-3-ol-2-one-5)-mercury (IV).

Found %: C 59.32, 59.29; H 5.09, 5.11; Hg 27.37. M 714.8. $C_{36}H_{34}O_4Hg$. Calculated %: C 59.13; H 4.65; Hg 27.45. M 730.6.

On determining the number of hydroxyl groups, low results were obtained (0.98, 0.76 or 2.30, 1.78% instead of 2 and 4.65%), probably because of the formation of a precipitate which enveloped the material.

Experiment 2. Mercuric acetate and the glycol in alcohol solution. 2 g of the glycol, 2.4 g of mercuric acetate (molar ratio 1 : 1), 20 ml 96% ethyl alcohol, 5 ml water were taken. On mixing these, heat was evolved and a colorless, slightly turbid solution was formed. The solution was heated to the boiling point of the alcohol for 5 hours. The solution gave an acidic reaction and smelled strongly of acetic acid. After evaporating the alcohol off, a white crystalline mass, which smelled of acetic acid, was obtained. The solid material was filtered off, washed several times with small portions of water and then aqueous alcohol and dried in air. The yield was 4.1 g (about 100%) of a fine crystalline powder, which was readily soluble in all organic solvents and slightly less in petroleum ether. It melted in the range 104-116° without decomposition. In an attempt to recrystallize it from petroleum ether, it separated in the form of an oil. It gave reactions for hydroxyl and carbonyl groups and probably was (II) (2-methyl-3,5-diphenyl-4-acetomercuripenten-3-ol-2-one-5).

Found %: C 48.06, 48.02; H 4.25, 3.95; Hg 37.82, 37.71. M 542, 536. $C_{20}H_{20}O_4Hg$. Calculated %: C 45.75; H 3.81; Hg 38.24. M 525.

The high carbon content and the slightly low mercury content and also the indistinctness of the melting point of the material was apparently caused by 2-hydroxydihydrofuran-2,5, as an impurity in the organomercury compound. The material with m.p. 109-116° immediately gave a 2,4-dinitrophenylhydrazone with m.p. 144° when treated with 2,4-dinitrophenylhydrazine in alcohol solution with sulfuric acid present. The melting point of the hydrazone obtained was not depressed on mixing with the hydrazone of (III), obtained from the glasslike material in experiment 1.

When the material with m.p. 109-116° was dissolved in methyl alcohol and treated with calcium chloride under the conditions in Experiment 1, a material with m.p. 155-156° was isolated, which did not depress the melting point of the product, obtained from calcium chloride treatment of the glasslike material, and had the same properties.

Experiment 3. Mercuric acetate and 5,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuran-2,5 in alcohol solution. A solution of 1 g of the 2-hydroxydihydrofuran-2,5 in 5 ml of alcohol was poured into a mixture of 1.25 g of mercuric acetate, 10 ml of 96% ethyl alcohol and 2.5 ml of water. Neither evolution of heat nor disappearance of the mercuric acetate occurred. During mixing for 15 minutes no change was observed. The mixture was heated for 5 hours while it was stirred and the alcohol boiled vigorously; the amount of mercuric acetate gradually decreased and at the end of the heating a colorless, almost clear solution was obtained with a strong smell of acetic acid. After evaporating off the alcohol in air, 1.9 g (96%) of a slightly grey, crystalline material, with m.p. 99-105°, was obtained, which was purified by washing with aqueous alcohol and a very small amount of ether. It was not possible to achieve a sharper melting point as the material was extremely soluble in all organic solvents and after evaporation, in an attempt at recrystallization, it separated as a thick oil (VI, 5,5-dimethyl-2,4-diphenyl-3-acetomercuri-2-hydroxydihydrofuran-2,5). The melting point was depressed on admixture with the organomercury material with m p. 99-105°, obtained by treatment of the acetylenic glycol with mercuric acetate.

Found %: C 47.01, 47.11; H 4.22, 4.44; Hg 39.01. M 554, 531. $C_{20}H_{20}O_4Hg$. Calculated %: C 45.75; H 3.81; Hg 38.24. M 525.

The analytical data and the indistinct melting point showed that the pure form of the organomercury compound had not been successfully isolated.

The 2,4-dinitrophenylhydrazone of the material with m.p. 99-105° separated at once as a orange-yellow precipitate. It decomposed at 144° and the melting point was not depressed by the 2,4-dinitrophenylhydrazones obtained in experiments 1 and 2 (III).

On treating the material with m.p. 99-105° with calcium chloride in methyl alcohol, a fine crystalline precipitate separated much more rapidly than in experiments 1 and 2. After washing, the precipitate melted at 200-202° and the melting point was not depressed by mixing with the heterocyclic symmetrization product, obtained by gaseous ammonia treatment of the solution of organomercuric compound from mercuric chloride treatment of the glycol [1]. The material did not react with methylmagnesium iodide, contained mercury, gave fluorescence with strong sulfuric acid and was soluble in the same solvents as the material with m.p. 203-204°.

Determinations of carbon and hydrogen in the organomercury compounds were carried out by M. I. Potapenko, to whom we are very grateful.

SUMMARY

1. By treating unsymm. dimethyldiphenylphenylacetylenylethyleneglycol with an alcohol solution of mercuric acetate, we succeded in separating an organomercury compound corresponding to the open form of 2-hydroxydihydrofuran – 2-methyl-3,5-diphenyl-4-acetomercuripenten-3-ol-2-one-5 which symmetrized by calcium chloride into 4-di-(2-methyl-3,5-diphenylpenten-3-ol-2-one-5)-mercury.

2. It was shown that, in contrast to mercuric chloride, mercuric acetate mercurates 5,5-dimethyl-2,4-diphenyl-2-hydroxydihydrofuran-2,5, forming 5,5-dimethyl-2,4-diphenyl-3-acetomercuri-2-hydroxydihydrofuran-2,5, which gives the same product of symmetrization by calcium chloride as the organomercury compound obtained by treating the glycol with mercuric chloride.

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Lensoviet Leningrad Institute
of Technology

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* T.p. = C. B. Translation pagination.

On treating the material with [illegible]

Determination of carbon and hydrogen in the organomercury compounds were carried out by M. I. [illegible], to whom we are very grateful.

SUMMARY

1. By treating [illegible]

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[illegible] Institute
of Technology

THE REACTION OF DIVINYL OXIDE WITH AMINES

A. A. Petrov and V. M Albitskaya

K. A. Krasusky [1] established in 1911 that ammonia and amines added to unsymmetrical organic α-epoxides with the formation of alcohols, containing a hydroxyl on the carbon with least hydrogens, that is in accordance with Markovnikov's rule [2]. In a series of recently published investigations it was shown by one of us that unsymmetrical α-epoxides, especially of the vinylethylene oxide type, add to various materials under certain conditions and in a reverse order to that prescribed by Markovnikov's rule [3]. The particular tendency of vinylethylene oxides to add in an anomalous manner is due to conjugation between the oxide and double bonds.

In the light of the above investigations, the study of the course of combination of divinyl oxide with ammonia and amines appeared very interesting.

The course of combination of divinyl oxide with ammonia had already been investigated [4]. It was established that in this case, unlike propylene oxide which has a similar structure, two isomeric amino alcohols were formed in a ratio of 6.5:1. The amino alcohol formed in accordance with Markovnikov's rule predominated.

The isomeric amino alcohols were separated as the oxalates which had different solubilities in dry ethyl alcohol.

The reactions of divinyl oxide with amines have hardly been studied at all. In the available articles [5] and patents [6, 7] on this problem, the products obtained were poorly characterized by the authors who, without proof, adopted formulas for them that conformed to the combination of amines with divinyl oxide by Markovnikov's rule.

We investigated the reactions of divinyl oxide with primary and secondary amines to characterize the addition compounds in more detail.

As a result of reactions of divinyl oxide with primary amines, from methylamine to butylamine, 5 alkylaminobutenols were obtained, whose constants are given in Table 1, where the melting points of the picrolonates

TABLE 1

Material	Boiling point, pressure (mm)	d_4^{20}	n_D^{20}	*MR*		Melting point of picrolonates
				found	calculated	
$CH_2{=}CH{-}CHOH{-}CH_2NHCH_3$ . . .	80.5—81° (20)	0.9282	1.4608	29.89	29.95	192—193°
$CH_2{=}CH{-}CHOH{-}CH_2NHC_2H_5$ . .	86—87 (20)	0.9114	1.4570	34.42	34.57	211—212 (decomp.)
$CH_2{=}CH{-}CHOH{-}CH_2NHC_3H_7$ . .	95—96 (20)	0.8991	1.4580	39.21	39.19	179—180
$CH_2{=}CH{-}CHOH{-}CH_2NHC_3H_7$- iso	89—94 (21)	—	1.4508*			
$CH_2{=}CH{-}CHOH{-}CH_2NHC_4H_9$ . .	108—109 (20)	0.8906	1.4588	43.94	43.80	181—182
$CH_2{=}CH{-}CHOH{-}CH_2N(CH_3)_2$.	57.5—58.5(20) 67—68(32 [6])	0.8939	1.4508	34.68	34.91	95—96
$CH_2{=}CH{-}CHOH{-}CH_2N(C_2H_5)_2$	76.5 (20) 71—72 (19)	0.8705 —	1.4470 1.4445[6]	43.96	44.14	109
$CH_2{=}CH{-}CHOH{-}CH_2N(C_3H_7)_2$ . .	101 (20)	0.8598	1.4480	53.33	53.38	81—82
$CH_2{=}CH{-}CHOH{-}CH_2N(C_4H_9)_2$ . .	127 (20)	0.8560	1.4508	62.67	62.61	98—99

derived from them are also given. Attempts to separate these picrolonates into possible isomers (by solubility) were unsuccessful. In each case it was possible to separate only one picrolonate. From this we concluded that the primary amines combined with divinyl oxide practically completely in accordance with Markovnikov's rule.

It can be seen from the data in Table 1 that with an increase in the molecular weight of the alkyl (in the limits C_{1-4}), the homologous difference in boiling points increases, the specific gravity falls and the refractive index changes very little. The picrolonates have high melting points, and for amines with even numbers of carbon atoms in the radical, they are somewhat higher than for amines of different structure.

As a result of combining divinyl oxide with four normal secondary amines (from dimethylamine to dibutylamine inclusively) 4 unsaturated amino alcohols were obtained, with the constants given in the same Table. In accordance with the arguments given above, a secondary alcohol formula was ascribed to them. It was impossible to find another isomer in the mixture due to the small quantity of picrolonate used.

As can be seen from the data in Table 1, the tertiary amino alcohols differed from the isomeric, secondary amino alcohols in their lower boiling points, specific gravity and refractive indices. The melting points of picrolonates in the tertiary amino series were considerably lower than for the secondary series and, as above, the effect of the number of carbon atoms was observed.

The addition of amines to divinyl oxide in the manner prescribed by Markovnikov's rule was, as was to be expected, and exception. In a series of papers one of us showed that an alkaline medium encouraged "normal" addition of various materials to unsymmetrical oxides, among them divinyl oxide [3]. The amines possess considerably greater basicity (by several orders) than ammonia and consequently must add in greater measure than ammonia in accordance with Markovnikov's rule and this fact was actually observed.

EXPERIMENTAL

Amines obtained from the Leina-verke factory were used in this experiment. Before being used they were distilled in a fractionating column. All the amines boiled within a range of 1°, and had constants similiar to those quoted in the literature.

Divinyl oxide was prepared from the chlorohydrin. The latter was prepared in its turn from pure divinyl (purity 99.8 %) by the method described earlier [8] and had the following constants:

B.p. 63.2° (30 mm), d_4^{20} 1.1123, n_D^{20} 1.4649.

90 g of divinyl oxide (88% when calculated on the initial chlorohydrin) was obtained from 160 g of divinyl chlorohydrin by treatment with caustic potash.

Found for the oxide: b.p. 67-68°, d_4^{20} 0.8751, n_D^{20} 1.4182.

One of us had previously given the following constants [8]: b.p. 67° (750 mm), d_4^{20} 0.8745, n_D^{20} 1.4182.

The divinyl oxide reaction with amines was carried out under the following conditions. Divinyl oxide (usually 0.2 mole) was added dropwise during vigorous stirring to excess aqueous amine solution (5-fold excess in the case of primary amines and 3-fold for secondary; the water was 35-40% of the solution in all cases). Heating was observed. After standing for 8-10 hours dry potash was added to the mixture, the upper layer was separated, it was treated several more times with potash, dried by potash and distilled in a Widmer fractionating column, first at regular pressure, then in vacuum. Low-boiling amines (methyl-, ethyl-, dimethylamines) distilled immediately on adding potash to the reaction mixture. In the case of dibutylamine all the distillation was carried out in vacuum.

The constants of the amino alcohols obtained are given in Table 1. The melting points of picrolonates obtained from them are also given. To obtain the latter a theoretical quantity of amino alcohol was added to an alcohol solution of picrolonic acid. The picrolonate deposit was filtered off and recrystallized from alcohol. In all cases the same picrolonate was also isolated from the mother liquor.

Yields and analytical data for the amino alcohols and their picrolonates are given in Table 2.

The small higher fractions obtained in all cases were not investigated further.

TABLE 2

Material	Yield (in %)	% N		Nitrogen content in the picrolonate (%)	
		found	calculated	found	calculated
$CH_2=CH-CHOH-CH_2NHCH_3$	65	14.26	13.85	18.77, 19.53	19.17
$CH_2=CH-CHOH-CH_2NHC_2H_5$	72	12.28	12.19	18.64, 18.78	18.46
$CH_2=CH-CHOH-CH_2NHC_3H_7$	83	10.57	10.84	17.96, 18.19	17.81
$CH_2=CH-CHOH-CH_2NHC_3H_7$-iso	80	10.68	10.84	—	—
$CH_2=CH-CHOH-CH_2NHC_4H_9$	82	10.14	9.78	17.41	17.19
$CH_2=CH-CHOH-CH_2N(CH_3)_2$	78	12.56	12.19	18.14	18.46
$CH_2=CH-CHOH-CH_2N(C_2H_5)_2$	84	9.44	9.78	17.17	17.19
$CH_2=CH-CHOH-CH_2N(C_3H_7)_2$	66	7.91	8.18	16.32	16.08
$CH_2=CH-CHOH-CH_2N(C_4H_9)_2$	86	7.09	7.03	15.40	15.11

SUMMARY

1. The reaction of divinyl oxide with primary amines (methyl-, ethyl-, propyl-, isopropyl- and butylamines) and secondary amines (dimethyl-, diethyl-, dipropyl- and dibutylamines) was investigated.

2. The corresponding amino alcohols were isolated and characterized. Characteristic picrolonates were obtained from amino alcohols with normal structure of the radical (in the amino group).

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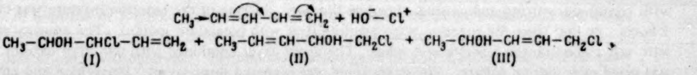
HYPOCHLORINATION OF PIPERYLENE*

A. N. Pudovik and B. E. Ivanov

The investigations carried out by B. A. Arbuzov and V. M. Zoroastrova [1], Kadesch [2] and A. A. Petrov [3] showed that hypohalous acids and their esters add to divinyl mainly in the 1,2 position, though not without exceptions, as was stated earlier [4]. The action of benzosulfodichloroamide on a solution of divinyl in ethyl alcohol resulted in the formation of about 12% of 1,4 addition compound [1]. In the case of the simultaneous action of ethylene oxide and chlorine on divinyl, 34% of 1,4-addition compound – β-oxyethylhypochlorite – was obtained. Kadesch established that hypochlorination of divinyl with chloride of lime resulted in 18.6% of hypochlorous acid addition in the 1,4 position [2]. The nature of the diene and the hypohalous ester and the reaction method and temperature substanially influenced the course of the addition [3]. The addition of hypohalous acids and their esters to divinyl halide derivatives may take place in the 1,4- and 3,4- positions [5]. The work of Oroschnik and Mallory [6] established that hypochlorous acid and its esters add to isoprene in the 1,2- and 1,4- positions.

The results of the investigation of the addition reaction of hypochlorous acid with piperylene are given in this article. The hypochlorination took place in an aqueous medium with chloride of lime [2]. This method has the advantage that a relatively small quantity of substitution products are formed and there is little chlorine addition to divinyl hydrocarbons. Piperylene chlorohydrins were separated from the dichloride and other chlorination products by washing the reaction mixture with water.

In accordance with the polarization of piperylene and hypochlorous acid it seems likely that the addition reaction would mainly follow the equation:



$$CH_3{\rightarrow}CH{=}CH{-}CH{=}CH_2 + H\overset{-}{O}{-}Cl^{+}$$

$$\underset{(I)}{CH_3{-}CHOH{-}CHCl{-}CH{=}CH_2} + \underset{(II)}{CH_3{-}CH{=}CH{-}CHOH{-}CH_2Cl} + \underset{(III)}{CH_3{-}CHOH{-}CH{=}CH{-}CH_2Cl},$$

with the formation of one, two or three isomeric glycol chlorohydrins. From piperylene hypochlorination we actually did obtain all three chlorohydrins: 3-chloropenten-1-ol-4 (I) with b.p. 50-51° (13 mm), n_D^{20} 1.4570, d_4^{20} 1.0564; 1-chloropenten-3-ol-2 (II) with b.p. 66-67° (15 mm), n_D^{20} 1.4665, d_4^{20}1.0720; 1-chloropenten-2-ol-4 (III) with b.p. 82-82.5° (13 mm), n_D^{20} 1.4760, d_4^{20} 1.0835.

The chlorohydrin separation was carried out by repeated distillation of the reaction mixture and separate fractions in a bubble-cap column with an efficiency of about 20 theoretical plates. The overall chlorohydrin yield was about 13% on piperylene used; the greater part of it was recovered unchanged from the reaction. Analysis results on chlorine content and calculation of molecular refractions showed that all 3 separated products were piperylene chlorohydrins. The presence of the hydroxyl group in the chlorohydrins was proved by preparing monochlorohydrin α-glycol acetates, using acetic anhydride. The action of aqueous alkali solution on the chlorohydrins (I) and (II) at 160° gave the corresponding piperylene α-epoxides; under similar conditions, no oxide was obtained from (III). By treating (I) and (III) with bromine, dibromides were obtained and characterized. The position of the double bond in the chlorohydrins was proved by their oxidation with potassium permanganate and ozonization. On ozonization and oxidation of chlorohydrin (I), formaldehyde (condensation product with β-naphthol with m.p. 188°) and formic acid respectively were separated and identified.

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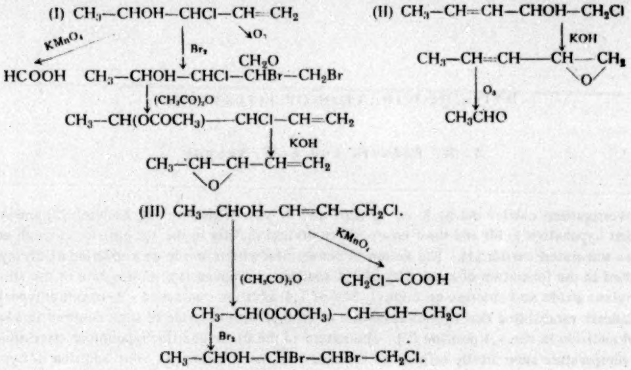
* Preliminary report: Proc. Acad. Sci. USSR 103, 443 (1955).

Acetaldehyde (2,4-dinitrophenylhydrazone with m.p. 155-156°) was obtained from ozonization of (II), and monochloroacetic acid by oxidizing (III) with potassium permanganate.

The reactions carried out can be represented by the following diagram:



A study of the hydrolysis kinetics of a 0.1 M aqueous chlorohydrin solution at 50° showed that after 8 hours 41 % of (I), 47% of (III) and 7% of (II) were saponified. The ease of saponification of (I) and (III) was due to their having chlorines in the allyl position; in (II) the chlorine atom was isolated from the double bond. The kinetic data likewise confirmed the structure of the chlorohydrins (I), (II) and (III). The results of this investigation show that hypochlorous acid adds to piperylene in the 1,2-, 3,4- and 1,4- positions.

EXPERIMENTAL

Hypochlorination of piperylene in an aqueous solution of chloride of lime. A strong current of carbon dioxide was passed through a suspension of 400 g of chloride of lime in 5 liters of water at 0° for 30 minutes with vigorous mechanical stirring. Then 400 g of piperylene was added to the reaction mixture in small portions over 3 hours, with continuous stirring and passing of carbon dioxide. Stirring of the reaction mixture was continued for a further 2 hours. By that time the reaction was complete (test with potassium iodide). The aqueous solution was saturated with salt and extracted 5 times with ether. The upper layer combined with the ether extract. The ether solution was dried over sodium sulfate. The experiment was repeated three times. Piperylene and ether were distilled off on a water bath. The weight of the residue was 230 g. Analysis for chlorine content on the residue showed that it was a mixture of piperylene chloride and chlorohydrin.

Found %: Cl 41.10. C_5H_9OCl. Calculated %: Cl 29.46. $C_5H_8Cl_2$. Calculated %: Cl 51.08.

To extract the chlorohydrin from the residue, it was washed 10 times with 100 ml portions of water. The aqueous solution of piperylene chlorohydrin was saturated with salt and extracted 5 times with ether. After drying over sodium sulfate, the ether was distilled off and the residue (145 g) was distilled under vacuum through a bubble-cap column with an efficiency of about 20 theoretical plates. The distillation was carried out at 30 mm pressure. 6 fractions were obtained: 1st up to 61°, 8 g; 2nd 61-62°, 30 g; 3rd 62-73°, 2.5g; 4th 73-74.5°, 13 g; 5th 74.5-92°, 4 g; 6th 92-92.5°, 25 g; residue 30 g.

A second distillation of the 2nd fraction gave 25 g of 3-chloropenten-4-ol-3.

B.p. 50-51° (13 mm), n_D^{20} 1.4570, d_4^{20} 1.0564, MR_D 31.07; Calcd. 31.25.
Found %: Cl 29.51. C_5H_9OCl. Calculated %: Cl 29.46.

7 g of 5-chloropenten-2-ol-4 were isolated by a second distillation of fractions 4 and 5.

B.p. 66-67° (15 mm), n_D^{20} 1.4665, d_4^{20} 1.0720, MR_D 31.16; Calcd. 31.25.
Found %: Cl 29.21. C_5H_9OCl. Calculated %: Cl 29.46.

A second distillation of fraction 6 gave 21 g of 5-chloropenten-3-ol-2.

B.p. 82-82.5° (13 mm), n_D^{20} 1.4760, d_4^{20} 1.0835, MR_D 31.30; Calcd. 31.25.

Found %: Cl 29.43. C_5H_9OCl. Calculated %: Cl 29.46.

Oxidation of 3-chloropenten-4-ol-2 with potassium permanganate. 58 g of finely powdered potassium permanganate was gradually added to 12 g of 3-chloropenten-4-ol-2 in 800 ml of water, which was cooled with water and stirred. The rate of addition was regulated so that the temperature of the reaction mixture did not rise above 15°. The precipitate of manganese dioxide was filtered off and washed with hot water and the filtrate was evaporated in vacuum and acidified with 50% sulfuric acid. The acid was separated by many extractions with ether. The ether extract was dried over calcium chloride and the ether was distilled off. The residue was twice distilled to give 3 g of formic acid (b.p. 101-102°, n_D^{20} 1.3960, d_4^{20} 1.2270). It had a sharp, characteristic smell and reduced ammoniacal silver nitrate solution.

Oxidation of 5-chloropenten-3-ol-2 with potassium permanganate. 58 g of finely powdered potassium permanganate was added with stirring to a solution of 12 g of 5-chloropenten-3-ol-2 and 40 g of magnesium sulfate in 400 ml of water. The reaction mixture was further treated as described above. Distillation of the residue gave 4 g of monochloroacetic acid. B.p. 175-180°; m.p. 60-61°.

Found %: Cl 37.36. $C_2H_3O_2Cl$. Calculated %: Cl 37.57.

Ozonolysis of 3-chloropenten-4-ol-2. 5 g of 3-chloropenten-4-ol-2 was dissolved in 50 ml of dry chloroform and a stream of oxonized oxygen was passed through it at 0° for 14 hours. The chloroform was distilled off under vacuum and the ozonide, in the form of a thick, glassy mass, was covered with 30 ml of ether and was left to stand overnight at room temperature. The ether was distilled off in vacuum and the ozonide was decomposed by gradually heating with water to 100° in a flask with a reflux condenser. Formaldehyde was identified in the form of methylene dinaphthol. The m.p. was 187-188° with slight decomposition (from alcohol) A mixed m.p. showed no depression.

Ozonolysis of 5-chloropenten-2-ol-4. A stream of ozonized oxygen was passed for 14 hours through a solution of 4 g of 5-chloropenten-2-ol-4 in 50 ml of chloroform. The procedure of the previous experiment was followed. The ozonide was decomposed by gradually heating to 100° with water. Acetaldehyde distilled off and was trapped in a solution of 2,4-dinitrophenylhydrazine. After recrystallization from alcohol, the 2,4-dinitrophonylhydrazone had m.p. 166-167 (and mixed m.p.).

The addition of bromine to 3-chloropenten-4-ol-2. 16 g of bromine in 10 ml chloroform was added to 12 g of 3-chloropenten-4-ol-2 dissolved in 15 ml chloroform, while cooling with ice. After standing for 2 hours, complete loss of color was observed. Vacuum distillation gave 20 g of 1,2-dibromo-3-chloropentanol-4 in the form of a very viscous liquid. B.p. 136-138° (15 mm), n_D^{20} 1.5470.

Found %: Cl + 2Br 70.15; $C_5H_9Br_2Cl$. Calculated %: Cl + 2Br 69.70.

The addition of bromine to 5-chloropenten-3-ol-2. 16 g of 1-chloro-2,3-dibromopentanol-4, in the form of a very thick liquid, was obtained from 12 g of 5-chloropenten-3-ol-2 and 16 g of bromine by the method described above. After standing for a short time at room temperature, it completely crystallized. B. p. 146-149° (15 mm), m.p. (from alcohol) 69-70°.

Found %: Cl + 2Br 70.02. $C_5H_9Br_2Cl$. Calculated %: Cl + 2Br 69.70.

Acetylation of 3-chloropenten-4-ol-2. The reaction mixture, composed of 8 g of 3-chloropenten-4-ol-2, 7.8 g of acetic anhydride and 20 ml of benzene, was heated under reflux on a water bath for 5 hours. The benzene and acetic acid were distilled off and the residue was distilled in vacuum. After 2 distillations, 6 g of 3-chloropenten-4-ol-2 acetate was obtained.

B.p. 66-67° (13 mm), n_D^{20} 1.4365, d_4^{20} 1.0604, MR_D 40.11; Calc. 40.61.

Found %: Cl 21.73. $C_7H_{11}O_2Cl$. Calculated %: Cl 21.85.

Acetylation of 5-chloropenten-3-ol-2. 10g of 5-chloropenten-3-ol-2 and 10 g of acetic anhydride, dissolved in 25 ml of benzene, were heated under reflux on a water bath at 80-90° for 5 hours. 7 g of 5-chloropenten-3-ol-2 acetate was obtained from the distillation.

B.p. 89-89-5° (13 mm), n_D^{20} 1.4555, d_4^{20} 1.0790, MR_D 40.76; Calc. 40.61.
Found %: Cl 21.87. $C_7H_{11}O_2Cl$. Calculated %: Cl 21.85.

Action of alkali on 3-chloropenten-4-ol-2. 12 g of 3-chloropenten-4-ol-2 was added dropwise to 100 ml of 60% aqueous potassium hydroxide solution, heated to 160°. The distillate obtained separated into two layers on standing; the upper layer was separated off and dried over sodium sulfate. 5.6 g of 2,3-epoxypenten-4 was obtained by distillation.

B.p. 82-83°, n_D^{20} 1.4135, d_4^{20} 0.8464, MR_D 24.77; Calc. 24.26.
Found %: C 71.14; H 9.48. C_5H_8O. Calculated %: C 71.43; H 9.52.

Action of alkali on 5-chloropenten-2-ol-4. 2.6 g of 1,2-epoxypenten-3 was obtained from 6 g of 5-chloropenten-2-ol-4 by the method described above.

B.p. 103-104°, n_D^{20} 1.4345, d_4^{20} 0.8750, MR_D 25.25; Calc. 24.26.
Found %: C 71.50; H 9.63. C_5H_8O. Calculated %: C 71.43; H 9.52.

Action of alkali on 5-chloropenten-3-ol-2. 12 g of 5-chloropenten-3-ol-2 was added to 100 ml of 60% aqueous potassium hydroxide solution heated to 150°. A considerable amount of resinous product was formed. The separation of any kind of reaction product was unsuccessful.

Kinetics of saponification of piperylene chlorohydrin. 1.205 g of each chlorohydrin was weighed into a 100 ml graduated flask. The graduated flasks were made up to the mark with water, heated to 50°, shaken until the sample dissolved completely and placed in a thermostat at 50 ± 0.3°. The concentration of Cl^- in samples withdrawn, was determined by Volhard titrations.

SUMMARY

1. It was shown that hypochlorous acid adds onto piperylene in the 1,2- 3,4- and 1,4-positions.

2. The following piperylene 3-chlorohydrins were isolated, characterized and their structures proved: 3-chloropenten-1-ol-4, 1-chloropenten-3-ol-2 and 1-chloropenten-2-ol-4.

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Kazan State University

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CONDENSATION OF DIENE HYDROCARBONS WITH ACETYLENEDICARBOXYLIC ACID AND ITS METHYL ESTER

N. P. Sopov and V. S. Miklashevskaya

A series of diene syntheses with the simplest acetylene aldehydes, ketones, acids, and esters was described earlier [1-4].

The simplest dibasic acetylene acid, acetylenedicarboxylic, and its esters have long been used for diene syntheses, but up to the present time only their reactions with divinyl [5] and cyclopentadiene [6], have been described, furthermore in the case of esters the products obtained were not completely characterized.

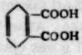
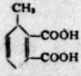
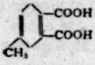
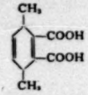
This investigation aimed at the study of the conditions and condensation products of the reactions of dimethyl acetylenedicarboxylate with divinyl, piperylene, isoprene and dipropylene.

The reactions were carried out in sealed glass tubes at 140-155° for 12 hours. In all cases the expected dihydrophthalic esters were isolated.

Dimethyl $\Delta^{1,4}$-dihydrophthalate had been obtained earlier [5], but had not been completely characterized. Esters of 6-methyl- $\Delta^{1,4}$-, 4-methyl- $\Delta^{1,4}$-, and 3,6-dimethyl- $\Delta^{1,4}$-dihydrophthalic acid-1,2 had not been described previously.

The dihydrophthalic esters were odorless and colorless viscous liquids. All were insoluble in water but dissolved well in benzene, chloroform and other organic solvents.

The constants of the materials obtained are shown in the table. The ester of 6-methyl-$\Delta^{1,4}$-dihydrophthalic acid showed exaltation of molecular refraction.

Acid	Melting point	Dimethyl esters			*MR*	
		Boiling point (10 mm)	d_4^{20}	n_D^{20}	found	calculated
	181—182°	138.5—139.5°	1.172	1.4950	48.83	48.55
	182—183	1st fraction 138.5—140.5	1.114	1.4886	54.45	53.17
	—	2nd fraction 141.5—142.5	1.124	1.4950	54.56	53.17
	192—193	151.5—152.5	1.142	1.4958	53.76	53.17
	191—192	1st fraction 141.5—143	1.120	1.4948	58.37	57.79
	—	2nd fraction 144—144.5	1.124	1.4965	58.33	57.79

One of us observed an analogous phenomenon for condensation products of piperylene with propargyl aldehyde which was explained by the isomerization of the original product into a compound with conjugated bonds. However, the attempt to confirm the presence of conjugated bonds by reaction with maleic anhydride was unsuccessful in this case.

The corresponding acids, of which only $\Delta^{1,4}$-dihydrophthalic acid [5] had been described previously, were obtained by the saponification of the dihydrophthalic methyl esters.

The saponification rate of the esters differed. Dimethyl $\Delta^{1,4}$-dihydrophthalate was saponified with ease, while the reaction with 3,6-dimethyl- $\Delta^{1,4}$-dihydrophthalic ester was considerably more difficult.

All the acids were white crystalline materials with high melting points. Difficultly soluble in benzene, ether, chloroform and cold water and easily soluble in alcohol and hot water. The acid melting points are given in the table.

It should be noted that it was considerably more convenient to synthesize $\Delta^{1,4}$-dihydrophthalic acid-1,2 and its homologs through their esters.

As can be seen from literature data [5] as well as from our experiments with isoprene, a considerable portion of the dibasic acid was decarboxylated during the condensation of diene hydrocarbons with acetylenedicarboxylic acid, and due to this the yield of dihydrophthalic acid was small. We isolated, among the other condensation products of acetylenedicarboxylic acid with isoprene, the anhydride of a corresponding dicarboxylic acid.

Dimethyldihydrophthalic acid was hydrogenated over Raney nickel. The amount of hydrogen consumed was close to the theoretical.

The synthesis of cyclohexadiene glycol from dimethyl dihydrophthalate by treatment with methyl magnesium iodide was unsuccessful. The hydrocarbons formed during distillation of the glycol in vacuum, were polymerized.

EXPERIMENTAL

The dimethyl ester of acetylenedicarboxylic acid was prepared by heating a solution of 40 g acetylenedicarboxylic acid in 220 ml of methyl alcohol with 12 ml of concentrated H_2SO_4 for 4 hours. Then the alcohol was distilled off and the residue was extracted with ether. After a preliminary wash with solutions of soda and $CaCl_2$ and drying over $CaCl_2$, the ether solution was distilled first at normal pressure on a water bath and then under vacuum. 27.5 g of dimethyl acetylenedicarboxylate was isolated:

B.p. 95-96° (19 mm), n_D^{25} 1.4490. Reported data [6]: b.p. 95-96° (19 mm), n_D^{25} 1.4444-1.4452.

Condensation with divinyl. 7.0 g of the ester and 10 ml of divinyl in 20 ml of toluene (0.1 g of hydroquinone) were heated at 140-145° in a sealed glass tube for 12 hours. The yield of condensation product was 7.5 g (74.9%, calculated on ester). The constants are given in the table.

Found %: C 61.12; H 6.12. $C_{10}H_{12}O_4$. Calculated %: C 61.22; H 6.16.

1.0 g of ester was heated under reflux for 2 hours with 0.82 g of NaOH (4 fold excess) in 7.5 ml of water. The solution was acidified with twice the calculated amount (relative to alkali taken) of 10% H_2SO_4, placed in a cooling mixture (ice salt) and kept there until it almost completely froze. After the solution had stood at room temperature for 12 hours, the white precipitate was filtered off. 0.57 g was obtained (65.8% of acid). The acid was recrystallized from water by freezing.

Found %: C 57.36; H 4.90. Equiv. 84.4. $C_8H_8O_4$. Calculated %: C 57.14; H 4.79. Equiv. 84.1.

Condensation with piperylene. 7.5 g of ester and 20 g of piperylene in 20 ml of toluene (+ hydroquinone) were heated at 150-155° for 12 hours. The yield of condensation product, with b.p. 136.5-144° (10 mm), was 9.4 g (84.8%). Two fractions were isolated by a second distillation: 1st 138.5-140.5°, 5 g; 2nd 141.5-142.5°, 3.2 g; residue 2.1 g (tar).

The constants of the 1st and 2nd fractions are given in the table.

Found (for 1st fraction) %: C 63.25, 63.12; H 7.16, 6.98. Found (for 2nd fraction) %: C 62.50; H 7.02. $C_{11}H_{14}O_4$. Calculated %: C 62.84; H 6.71.

1.2 g of ester (1st fraction) was heated with 0.93 g of NaOH in 8.5 ml of water for 3 hours. 6-Methyl-$\Delta^{1,4}$-dihydrophthalic acid was isolated by the method described above. The yield was 0.65 g (62.5%).

Found %: C 58.75; H 5.53. Equiv. 90.6. $C_9H_{10}O_4$. Calculated %: C 59.34; H 5.53. Equiv. 91.1.

0.5 g of acid and 2.0 ml of acetic anhydride were heated in a sealed glass tube on a water bath for 3 hours. On cooling the solution, 0.12 g of 6-methyl-$\Delta^{1,4}$-dihydrophthalic anhydride with m.p. 140-141°, was isolated.

Found %: C 65.42; H 4.67. $C_9H_8O_3$. Calculated %: C 65.84; H 4.91.

Condensation with isoprene. 7.0 g of ester and 4 g of isoprene in 20 ml of toluene (+ hydroquinone) were heated at 150° for 12 hours. The yield of condensation product was 8.9 g (86.7%). The constants are given in the table.

Found %: C 63.11, 63.13; H 6.48, 6.02. $C_{11}H_{14}O_4$. Calculated %: C 62.84; H 6.71.

1.0 g of ester was heated for 2 hours with 0.76 g of NaOH in 7 ml of water. Subsequent treatment of the reaction mixture gave 0.4 g (46.2%) of acid.

Found %: C 59.16; H 5.97. Equiv. 90.88. $C_9H_{10}O_4$. Calculated %: C 59.34; H 5.53. Equiv. 91.08.

Condensation with dipropenyl. 8 g of ester and 10 g of dipropenyl in 20 ml of toluene (+ hydroquinone) were heated at 150-155° for 12 hours. The yield of product was 9.5 g (67.3%). By distillation under vacuum twice, two fractions were isolated: 1st 141.5-143°, 3.9 g; 2nd 144-144.5°, 4 g residue (tar) 1.1 g.

The constants of the 1st and 2nd fractions are given in the table.

Found %: (for 1st fraction): C 64.61; H 7.12. $C_{12}H_{16}O_4$. Calculated %: C 64.27; H 7.19.

3.0 g of ester (a mixture of the two fractions) and 2.2 g of NaOH in 19 ml of water were heated for 5 hours. After acidification with 10% H_2SO_4 and cooling the solution, white crystals and an oily layer separated. Further cooling of the latter gave a few more of the same crystals. The material was recrystallized from water. The yield was 0.65 g (24.8%).

Found %: C 61.32; H 6.27. Equiv. 98.2. $C_{10}H_{12}O_4$. Calculated %: C 61.36; H 6.17. Equiv. 98.1.

0.517 g of acid in 70 ml of methyl alcohol was hydrogenated in presence of Raney nickel. 136 ml H_2 (22.5° 759mm) was taken up. The theoretical amount of H_2 is 118.18 ml.

Condensation of acetylenedicarboxylic acid with isoprene. 3.5 g of acid and 2 g of isoprene in 10 ml of toluene (+ hydroquinone) were heated at 170° for 6 hours. On opening, the tube was found to be under pressure. On cooling the residue, obtained after distilling off the toluene, we obtained 0.1 g of 4-methyl-$\Delta^{1,4}$-dihydrophthalic anhydride with m.p. 111.5-112° (from benzene).

Found %: C 65.56; H 4.57. $C_9H_8O_3$. Calculated %: C 65.85; H 4.91.

SUMMARY

1. The condensation of divinyl, piperylene, isoprene and dipropenyl with dimethyl acetylenedicarboxylate was investigated.

2. From the esters of $\Delta^{1,4}$-dihydrophthalic acid and its homologs, obtained in this way, the corresponding acids and anhydrides were prepared.

3. It was shown that the preparation of dihydrophthalic acid and its homologs proceeds more easily from acetylenedicarboxylic esters than from the acid itself, as in the latter case decarboxylation and other processes take place.

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Institute of Aviation
Instrument Construction

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INVESTIGATION IN THE FIELD OF CONJUGATED SYSTEMS

LXIV. THE ACTION OF BENZOSULFODIBROMOAMIDE ON SOLUTIONS OF PIPERYLENE IN METHYL AND ETHYL ALCOHOLS

T. A. Zyryanova and A. A. Petrov

It was shown previously [1] that piperylene adds alkylhypochlorites in the 1,2- and 1,4-positions when treated with alcohol solutions of benzosulfodichloroamide. The ratio between these isomeric chloroethers is of the order 5-6:4, furthermore, the position of initial attack (fixation position of the chlorine atom) is the terminal (fourth) atom of the conjugated system.

Piperylene thus differs markedly from divinyl in the addition order of alkylhypochlorites. Divinyl, under the same conditions, produces only about 10% of 1,4-products [2]. The high polarity of piperylene is, apparently, the reason for its increased yield of 1,4-products.

In the light of this data, the investigations of the addition order of alkylhypobromites to piperylene was undoubtedly interesting. These add to divinyl almost exclusively in the 1,2-position [2]. With this aim, we studied the action of benzosulfodibromoamide on piperylene in methanol and ethanol solutions.

As in the case of alkylhypochlorites, the formation of 6 isomeric bromoethers would be expected:

$CH_3-CH=CH-CH(OR)-CH_2Br$; (I) $CH_3-CH(OR)-CHBr-CH=CH_2$; (IV)
$CH_3-CH=CH-CHBr-CH_2OR$; (II) $CH_3-CH(OR)-CH=CH-CH_2Br$; (V)
$CH_3-CHBr-CH(OR)-CH=CH_2$; (III) $CH_3-CHBr-CH=CH-CH_2OR$. (VI)

A small initial fraction and a main bromoether fraction with a rather narrow boiling range, but with a somewhat high alkoxyl and a correspondingly low bromine content, was obtained by distilling the reaction products.*

The low-boiling fraction contained a very small quantity of bromine and ether groups. The characteristic methyl propenyl ketone 2,4-dinitrophenylhydrazone was produced by treatment with 2,4-dinitrophenylhydrazine in acetic acid.

It was thus established that during the process of preparing and separating the bromoethers, a partial dehalogenation of the bromoethers (I) apparently took place with the formation of enol ethers $CH_3-CH=CH-C(OR)=CH_2$ (VII), which were then hydrolyzed to methyl propenyl ketone.

A study of the chemical reactions of the main fractions (bromoethers) showed that they consisted of mixtures of the isomeric bromoethers (I) and (V), with (I) as the main component.

1. Acetic and bromoacetic acids were isolated from the decomposition products of ozonides, obtained from the initial bromoether mixtures under the usual conditions. Acetic acid was determined as the silver salt and the bromoacetic was separated in a pure state and analyzed. Formaldehyde and formic acid were practically nonexistent.

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* It is possible that the mixtures with no halogen content were diethers of an unsaturated glycol. They could have formed as a result of bromoether alcoholysis (V). However, cases where hydrogen was replaced by alkoxyls during bromoalkoxylation have been described in the literature [3].

Acetic acid could have formed from the isomers (I) and (II). Bromoacetic acid could be obtained only from the bromoether (V). The absence of formaldehyde and formic acid in the ozonization products indicated that formation of isomers (III) and (IV) virtually did not take place.

2. When heated with alcoholic alkali the bromoethers gave mixtures of enol ethers (VII) and diethers of an unsaturated glycol:

$$CH_3CH(OR)-CH=CH-CH_2-CH_2OR \text{ (VIII)}$$

in a molar ratio of approximately 2.5:1. We have already described the materials (VII) and (VIII) in a previous report [1]. The ethers (VII) were obtained from bromoethers in a purer state than from chloroethers: they distilled within a range of 0.5-1° and dissolved completely in a few minutes in 5 % H_2SO_4 with the formation of methyl propenyl ketone.

A small initial fraction, obtained by distilling (VII), did not dissolve completely in sulfuric acid: however, it formed the same ketone. We were convinced of this by preparing the corresponding 2,4-dinitrophenylhydrazone. We used two piperylene samples: a pure cis-isomer and a cis- and trans-isomer mixture, containing about 75% of the latter material.

Materials (VII) that were pure cis-compounds and mixtures of cis- and trans- forms, with a considerable predominance of the latter, were obtained from the two piperylene samples respectively.

Two methyl propenyl ketone samples were obtained by hydrolysis. The material obtained from cis-piperylene could hardly be considered as a pure cis-isomer as slight interconversion between cis- and trans-isomers was possible in the given case through the enol form. The constants of the diene ethers obtained are compared in the table with those of unsaturated diene ethers [4].

Material	Boiling point	d_4^{20}	n_D^{20}	MR found	MR calculated
$CH_2=C(OCH_3)-CH=CH_2$	74—75°	0.8272	1.4432	26.94	26.00
$CH_2=C(OCH_3)-CH=CH-CH_3$ . .	106.5—107.5	0.8350	1.4555	31.92	30.61
$CH_2=C(OCH_3)-CH=CH-CH_3$-cis	105—105.5	0.8403	1.4570	31.81	30.61
$CH_2=C(OC_2H_5)-CH=CH_2$	93—94	0.8177	1.4450	31.94	30.61
$CH_2=C(OC_2H_3)-CH=CH-CH_3$ . .	124.5—125.5	0.8244	1.4490	36.49	35.23
$CH_2=C(OC_2H_5)-CH=CH-CH_3$-cis	124—124.5	0.8294	1.4530	36.55	35.23

It is very noticeable that the refractive indices and the values for molecular exaltation are considerably greater for the materials obtained from piperylene. The cis-ethers differ in having lower boiling points and greater specific gravities and refractive indices.

The diene-enol ethers (VII) can be formed only from bromoethers (I). Thus, data on alcoholic alkali treatment of the bromoethers proved the predominance of this isomer in the addition products of alkylhypobromites to piperylene. The diether (VIII) could be formed from (II), (IV), (V) and (VI) isomeric bromoethers with or without allylic rearrangement. The presence of bromoethers of isomer (IV) in the mixture was excluded by the ozonization data. The absence of isomers (II) and (VI) in the mixture is proved below. Thus, the diether of the unsaturated glycol (VIII) could have been obtained only from (V).

3. Hydrogenation of the initial bromoether mixtures over Raney nickel under pressure and at room temperature formed: 1) mixtures of ethers of methylpropenylcarbinol and secondary amyl alcohol (IX) and 2) mixtures of saturated bromoethers $C_3H_7-CH(OR)-CH_2Br$ (X) and (I). Material (IX) was purified by additional hydrogenation over colloidal palladium, material (X) was purified from the original unsaturated bromoether by additional hydrogenation and bromination.

The structure of the ethers of secondary amyl alcohols was determined by comparing their properties with those of pure materials obtained by other means. These ethers could have been formed by hydrogenation of the bromoethers (I), (IV) and (V). It was shown by a special experiment that bromoether (I) does not lose bromine under the hydrogenation conditions we chose. Thus, ethers (IX) could have been formed only from bromoethers (V).

The structure of the methyl bromoether (X) was determined by its conversion to the methyl ether of the enol form of methyl propyl ketone by alcoholic alkali. Methyl propyl ketone was obtained by hydrolytic cleavage of this ether. The structure of the ethyl bromoether (X) was determined by its conversion to pentene-1 with zinc dust.

The unsaturated bromoethers (X) could have been formed only from the unsaturated bromoethers (I). The ratio of (IX) and (X) shows that the isomers (I) and (V) were approximately in the ratio 2.5-3 : 1 in the initial bromoether mixtures, which coincides with the data in the previous section. It was thus established that alkylhypobromites add to piperylene in the 3,4-position to a greater extent than do alkylhypochlorites. At the same time, as in the case of alkylhypochlorite addition, piperylene shows a much greater tendency than divinyl to form 1,4-products. We had already noted [1] the high polarity of the fourth carbon atom in a piperylene molecule which causes halogen atoms to add predominately in this position.

EXPERIMENTAL

The Action of Benzosulfodibromoamide on Methyl Alcohol Solutions of Piperylene

a) For the work we used piperylene (b.p. 42-43°, d_4^{20} 0.6746, n_D^{20} 1.4320) containing about 70-75% of the trans-form. The reaction conditions and the method of product isolation were those described in the previous paper for preparing and separating chloroethers.

83 g of crude product were obtained from 68 g of piperylene and 94.5 g of benzosulfodibromoamide in 250 ml of methyl alcohol. The piperylene was distilled off on a water bath. The residue weighed 56 g. Distillation of this in a vacuum of 20 mm (25 cm Widmer fractionating column) gave the following fractions: 1st up to 50°, 2.7 g; 2nd 50-55°, 1.0 g; 3rd 55-65°, 4.2 g; 4th 65-67.5°, 19.7 g; 5th 67.5-69.5°, 17.3 g; 6th 69.5-71°, 3.6 g; residue 3.5 g.

The 1st fraction distilled at 122-125° at atmospheric pressure.

d_4^{20} 0.8896, n_D^{20} 1.4498.
Found %: Br 5.18; OCH_3 10.42.

Treatment of this fraction with an acetic acid solution of 2,4-dinitrophenylhydrazine gave the 2,4-dinitrophenylhydrazone of methyl propenyl ketone with m.p. 157-158° (from ethyl alcohol). A sample mixed with authentic 2,4-dinitrophenylhydrazone of methyl propenyl ketone melted at the same temperature.

The 4th fraction (d_4^{20}1.2183, n_D^{20} 1.4626) was distilled again at the same pressure; 8.7 g came at 67-70°.

d_4^{20} 1.2432, n_D^{20} 1.4656.
Found %: Br 41.91, 42.42. $C_6H_{11}OBr$. Calculated %: Br 44.63.

The 5th fraction (d_4^{20}1.2619, n_D^{20} 1.4694) was analyzed for Br and OCH_3.

Found %: Br 43.39, 43.46; OCH_3 18.55, 18.76. $C_5H_8OCH_3Br$. Calculated %: Br 44.63; OCH_3 17.31.

Br and OCH_3 were also determined for the 6th fraction (d_4^{20}1.2790, n_D^{20} 1.4731) .

Found %: Br 43.99, 44.13; OCH_3 17.81, 18.14.

To determine the structures of the bromoethers of the 4th, 5th and 6th fractions, derivatives were prepared.

Ozonization. 9 g of material was taken for ozonization. Formaldehyde was not formed (test as dinaphthomethane) in a test sample of the oxonides. The products from normal decomposition of the oxonides were oxidized with $KMnO_4$. 4 g of acids was isolated from the solution obtained. The acids were separated into two fractions: 1st b.p. 56-60° (100 mm), 1.55 g and the 2nd b.p. 100-110° (10 mm), 2.15 g.

A silver salt was prepared from the 1st fraction.

Found %: Ag 64.52. $C_2H_3O_2Ag$. Calculated %: Ag 64.63.

On cooling, the second fraction crystallized. The crystals were collected, washed with petroleum ether and recrystallized from the same solvent. M.p. 48-49°.

Found %: Br 58.03. $C_2H_3O_2Br$. Calculated %: Br 57.55.

Action of alcoholic alkali. 56 g of bromoether was heated for 9 hours with 28 g of KOH (threefold excess) in 180 ml of methyl alcohol. By the method described earlier [1], an oil was isolated from the mixture obtained and this was distilled in vacuum at 100 mm to give the following two parts: 1st up to 85° (mainly at 44-45°), 10.8 g; 2nd 85-90°, 6.1 g.

Distillation of the 1st part at normal pressure gave the following fractions: 1st up to 106.5°, 1.0 g; 2nd 106.5-107°, 7.5 g; residue 1.0 g.

The material with b.p. 106.5-107° had the constants given in the table.

Found %: C 73.51; H 9.86; OCH_3 31.80, 31.30. $C_5H_7OCH_3$. Calculated %: C 73.42; H 10.27; OCH_3 31.62.

On shaking with 50 ml of 5% H_2SO_4, 5 g of ether dissolved in a few minutes with slight heating. Methyl propenyl ketone (2.1 g) was salted out from the mixture obtained with $(NH_4)_2SO_4$.

B.p. 120-121°, d_4^{20} 0.8654, n_D^{20} 1.4355. 2,4-dinitrophenylhydrazone melted 157-158° (from alcohol).

Found %: N 21.57. $C_{11}H_{12}O_4N_4$. Calculated %: N 21.21.

Literature data for methyl propenyl ketone [5,6]: b.p. 122°, d_4^{20}0.8624, n_D^{20} 1.4350; 2,4-dinitrophenylhydrazone; m.p. 158°.

By distilling the 2nd part at 20 mm, the following fractions were obtained: 1st up to 53°, 0.6 g; 2nd 53-55°, 2.2 g; 3rd 55-56°, 1.6 g; 4th 56-67°, 1.71 g.

All the fractions had specific gravities greater than one and contained bromine. Therefore the material was again treated with alcoholic KOH, after which a fraction with b.p. 53-56° had d_4^{20}0.9058, n_D^{20} 1.4250 (1.5g).

Found %: OCH_3 47.52. $C_5H_8(OCH_3)_2$. Calculated %: OCH_3 47.68.

The constants for pure penten-2-diol-1,4 dimethyl ether had been found earlier [1]: b.p. 52.5-53.5, (20 mm), d_4^{20} 0.8898, n_D^{20} 1.4220.

Hydrogenation. 58 g of bromoether mixture with b.p. 61-67° (20 mm) was dissolved in 200 ml of CH_3OH, mixed with 25 g of $CaCO_3$ and 20 g of Raney nickel (paste) and hydrogenated in an autoclave at an initial pressure of 70 atm. for 6 hours at room temperature (15°). The reaction product was divided into two parts by distillation through a Widmer fractionating column: 1st up to 95° (at atmospheric pressure), 5.8 g; 2nd 63-66° (at 20 mm), 28.0 g.

When distilled again, the 1st part came over mainly at 87-90° and had d_4^{20} 0.7770, n_D^{20} 1.3993.

On hydrogenating 2.22 g of this material over colloidal Pd (5 mg) in 50 ml CH_3OH, 459 ml of H_2 (20°, 756.5 mm) was taken up. This gave the methyl ether of secondary amyl alcohol:

B.p. 88-88.5°, d_4^{20} 0.7548, n_D^{20} 1.3845, MR 31.66. $C_6H_{14}O$. Calcd. 31.55.

A sample, obtained by alkylating secondary amyl alcohol, had [1]: b.p. 88-88.5, d_4^{20} 0.7564, n_D^{20} 1.3840.

The 2nd part was separated into the following fractions by distillation: 1st up to 63°, 1.7 g; 2nd 63-65°, 13.5 g (d_4^{20} 1.2180, n_D^{20} 1.4572); 3rd 65-66°, 14.5 g (d_4^{20}1.2660, n_D^{20} 1.4650); 4th residue 1 g.

By a second hydrogenation (all the fractions were combined) under the same conditions, a product was obtained which started to boil at 150° at normal pressure. Distillation of the material at 20 mm gave the following fractions: 1st up to 63°, 2.21 g; 2nd 63-63.5°, 12.3 g (d_4^{20} 1.2351, n_D^{20} 1.4515); 3rd 63.5-64°, 6.2 g (d_4^{20} 1.2464, n_D^{20} 1.4530); residue 3.8 g.

The second and third fractions were combined (17 g) and brominated in chloroform with a 10% solution of bromine until decolorization no longer occured. 2 g of bromine was taken up and this corresponded to a 13% content of unsaturated bromoether. The saturated bromoether was distilled off from the tribromide through a Widmer column. Fractions obtained: 1st up to 63°, 3.2 g; 2nd 63.5-64°, 10 g; 3rd 64-65°, 1.4 g; residue 1.3 g.

Found for fraction from 63.5-64° at 20 mm:

d_4^{20} 1.2410, n_D^{20} 1.4509, MR 39.28. $C_6H_{13}OBr$. Calcd. 39.32.

Found %: C 40.03; H 7.34; Br 43.72; OCH_3 17.23. $C_6H_{13}OBr$. Calculated %: C 39.79; H 7.23; Br 43.72; OCH_3 17.13.

14.5 g of bromoether was heated with a three fold excess of 25% KOH solution in methanol for 7 hours. After working up the mixture in the usual way, 5 g of enol ether was obtained:

B.p. 89-90°, d_4^{20} 0.7917, n_D^{20} 1.4062. For this ether the following constants were found earlier: b.p. 89-90°, d_4^{20} 0.7888, n_D^{20} 1.4062.

A solution of 2,4-dinitrophenylhydrazine in acetic acid was added to a small amount of the material. Methyl propyl ketone 2,4-dinitrophenylhydrazone with m.p. 141° precipitated from the mixture.

b) Cis-piperylene (b.p. 43-44°, d_4^{20} 0.6912, n_D^{20} 1.4362).was used for the experiments. The material was obtained from a mixture of piperylenes by heating with maleic anhydride and subsequent distillation.

The following constants are reported in the literature for pure cis-piperylene [6]: b.p. 44.07°, d_4^{20} 0.6910, n_D^{20} 1.4363 [7].

From 76 g of cis-piperylene and 100 g of benzosulfodibromoamide in 300 ml of methyl alcohol was obtained 65 g of an oil, which was separated into the following fractions by distillation at 10 mm: 1st up to 48°, 9 g; 2nd 53-55°, 16.2 g; 3rd 55-57°, 24.42 g; 4th 57-62°, 6 g; residue 3 g.

For fraction with b.p. 53-55° (10 mm): d_4^{20} 1.1972, n_D^{20} 1.4618.

Found %: Br 43.01, 43.10; OCH_3 19.20. $C_5H_8OCH_3Br$. Calculated %: Br 44.63; OCH_3 17.33.

For fraction with b.p. 55-57° (10 mm): d_4^{20} 1.2612, n_D^{20} 1.4700.

Found %: Br 43.65, 43.71; OCH_3 18.49. $C_5H_8OCH_3Br$. Calculated %: Br 44.63; OCH_3 17.33.

48 g of fractions 2, 3 and 4 was heated for 9 hours with 45 g KOH (three fold excess) in 100 ml of methyl alcohol. 15.1 g of enol ether and 7.6 g of ether diol were isolated from the solution obtained. The constants of the enol ether are given in the table.

Found %: C 73.44; H 10.29; OCH_3 31.41. $C_5H_7OCH_3$. Calculated %: C 73.42; H 10.27; OCH_3 31.62.

Methyl propenyl ketone was obtained from the ether.

B.p. 116-119°, d_4^{20} 0.8593, n_D^{20} 1.4348.

Found %: C 71.29; H 9.53. C_5H_8O. Calculated %: C 71.40; H 9.59.

The 2,4-dinitrophenylhydrazone of the ketone melted at 154° (from alcohol).

Found for penten-2-diol-1,4 dimethyl ether:

B.p. 52-53°, d_4^{20} 0.8754, n_D^{20} 1.4235, MR 37.84. $C_7H_{14}O_2$. Calcd. 37.34.

Found %: C 64.78; H 11.25; OCH_3 47.47. $C_5H_8(OCH_3)_2$. Calculated %: C 64.58; H 10.84; OCH_3 47.68.

Action of Benzosulfodibromoamide on an Ethyl Alcohol Solution of Piperylene

a) The cis-trans-piperylene mixture characterized in the previous section was used for the experiment. 98.7 g of a mixture of bromoethers was obtained from 136 g of piperylene and 190 g of benzosulfodibromoamide in 600 ml of ethyl alcohol. Distillation of this mixture gave the following fractions: 1st up to 64°, 15 g; 2nd 64-69°, 7.0 g (n_D^{20} 1.4552); 3rd 69-72°, 53.6 g (n_D^{20} 1.4585); 4th 74-80°, 2.0 g (n_D^{20} 1.4667); residue 8.1 g.

For the 3rd fraction:

Found %: Br 40.14; OC_2H_5 26.10, 26.19. $C_5H_8OC_2H_5Br$. Calculated %: Br 41.39; OC_2H_5 23.34.

Ozonization. 10.0 g of the third fraction was ozonized, the ozonides were decomposed with water and the products were reoxidized with permanganate. Two acids were extracted with ether from the solution obtained: acetic and bromoacetic.

The acetic acid boiled at 50-60° (100 mm); its silver salt was analyzed.

Found %: Ag 64.24. $C_2H_3O_2Ag$. Calculated %: Ag 64.63.

The bromoacetic acid boiled at 105° (10 mm) and melted at 47-48.5° (from petroleum ether). A sample mixed with authentic bromoacetic acid melted at the same temperature.

Found %: Br 57.20. $C_2H_3O_2Br$. Calculated %: Br 57.55.

Action of alcoholic alkali. The action of alcoholic alkali was studied for the 2nd and 3rd fractions separately.

16 g of the 2nd fraction was treated with 20 g of KOH (three fold excess) in 80 ml of methyl alcohol (18 hours) under the conditions described earlier and gave 5.6 g of an oil, which was separated by distillation at 100 mm into a fraction 65-68°, 3.2 g and a residue of 1.8 g.

54 g of the 3rd fraction was treated with 48 g of KOH in 130 ml of methyl alcohol (18 hours) to give 28 g of an oil, which was separated by distillation at 100 mm into the following fractions: 1st 65-70°, 14.5 g; 2nd 70-80°, 1.2 g; residue 9.2 g.

The fractions up to 70° (100 mm) were combined and distilled at normal pressure with a Widmer fractionating column. Results of the distillation: 1st up to 122°, 0.5 g; 2nd 122-124.5°, 1.7 g; 3rd 124.5-125.5°, 10.8 g; 4th 125.5-128°, 2.0 g; residue 1.3 g.

The constants of the main material (fraction 124.5-125.5°) are given in the table.

Found %: C 74.82; H 10.61; OC_2H_5 40.55, 40.40. $C_5H_7OC_2H_5$. Calculated %: C 74.96; H 10.78; OC_2H_5 40.17.

Saponification of the ether with 5% H_2SO_4 gave methyl propenyl ketone; its 2,4-dinitrophenylhydrazone melted at 156-157°.

Both of the residues with boiling points above 70° (100 mm) were combined and distilled at 20 mm. This gave the following fractions: 1st 50-60°, 1.4 g; 2nd 65-68°, 5.3 g; 3rd 68-79°, 2.8 g; residue 0.7 g.

Found for fraction 65-68° (20 mm):

d_4^{20} 0.8889, n_D^{20} 1.4250, MR 41.41; Calcd. 41.96.

Found %: C 66.58; H 11.19. $C_8H_{16}O_2$. Calculated %: C 66.63; H 11.18.

Hydrogenation. 63 g of the mixture of bromoethers with b.p. 62-68° (10 mm) was hydrogenated in 200 ml of methanol in the presence of 100 g of sodium acetate and 33 g of Raney nickel (paste) for 6 hours with an initial hydrogen pressure of 70 atm. This gave 7.5 g of a mixture of saturated and unsaturated ethers not containing halogen with b.p. 105-108° (d_4^{20} 0.7773, n_D^{20} 1.3940 and 30 g of bromoethers with b.p. 59-60° (10 mm).

On hydrogenating 5 g of the ethers which did not contain halogen, 250 ml of hydrogen was taken up (in the presence of colloidal palladium). Found for the ethyl ether of secondary butyl alcohol obtained:

B.p. 105-106°, d_4^{20} 0.7565, n_D^{20} 1.3880. The constants for this material were reported earlier [1]: b.p. 105-106°, d_4^{20} 0.7635, n_D^{20} 1.3918.

On bromination of 29.5 g of the bromoethers, 1.4 g of bromine was taken up, which corresponds to approximately a 6% content of the initial unsaturated ether. After distillation from the products of bromination, the material had b.p. 58-59° (10 mm), 82° (34 mm), which corresponds to literature data [8].

Treatment of 25 g of the bromoether with 35 g of zinc dust in a water-alcohol medium under the usual conditions [8] gave about 5 g of pentene-1.

B.p. 29.5-30.5°, d_4^{20} 0.6422, n_D^{20} 1.3722.

Reported values [9]: pentene-1; b.p. 30°, d_4^{20} 0.6405, n_D^{20} 1.3715; pentene-2 b.p. 36.3-36.9°, d_4^{20} 0.6505, n_D^{20} 1.3808.

The material was ozonized. In the products of decomposition of the ozonide were found: formaldehyde (determined in a sample of the ozonide as dinaphtholmethane; m.p. 184°), formic acid (calomel test) and butyric acid (by smell). Acetic acid was not found (lanthanum test).

b) Cis-piperylene with the constants reported above, was used for the experiment. 55.7 g of a mixture of bromoethers was obtained from 69 g of cis-piperylene and 90 g of benzosulfodibromoamide in 250 ml of ethyl alcohol.

Distillation of the bromoethers at 10 mm gave the following fractions: 1st up to 60°, 6.2 g; 2nd 60-63°, 5.4 g; 3rd 64-66°, 15 g; 4th 66-69°, 15.1 g; residue 4.6 g.

The 3rd fraction had d_4^{20} 1.1877, n_D^{20} 1.4630.

Found %: Br 38.31, 38.26; OC_2H_5 25.15. $C_5H_8OC_2H_5Br$. Calculated %: Br 41.39; OC_2H_5 23.34.

The 4th fraction had d_4^{20} 1.1923, n_D^{20} 1.4648.

Found %: Br 39.93, 40.22; OC_2H_5 24.47. $C_5H_8OC_2H_5Br$. Calculated %: Br 41.39 OC_2H_5 23.34.

Treatment of 34 g of the 2nd, 3rd and 4th fractions with a solution of 30 g of KOH in ethyl ether (100 ml) gave 11.5 g of enol ether and 6.2 g of the diethyl ether of an unsaturated glycol. The constants of the enol ether are given in the table.

Found %: C 75.29; H 11.16; OC_2H_5 40.23. $C_5H_7OC_2H_5$. Calculated %: C 74.96; H 10.78; OC_2H_5 40.17.

The diethyl ether of the unsaturated glycol had the constants:

B.p. 75-76°:(20 mm), d_4^{20} 0.8610, n_D^{20} 1.4255, MR 47.04; Calcd. 46.58.

Found %: OC_2H_5 57.10. $C_5H_8(OC_2H_5)_2$. Calculated %: OC_2H_5 56.95.

SUMMARY

1. The action of benzosulfodibromamide on solutions of piperylene (a cis-trans mixture and pure cis-form) in methyl and ethyl alcohols has been investigated.

2. It was shown that the main products of the reaction were mixtures of ethers of 1-bromopenten-3-ol-2 (3,4-addition) and 1-bromopenten-2-ol-4 (1,2-addition) in the molar proportions of approximately 2.5 – 3:1.

3. From the 1-bromopenten-3-ol-2 ethers were obtained: 1) ethers of the enol form of methyl propenyl ketone (a mixture of cis- and trans-forms and pur cis-form) – by alcoholic alkali treatment, 2) ethers of 1-bromopentanol-2 – by reduction over Raney nickel. Treatment of the methyl ether of bromopentanol with alcoholic alkali gave the methyl ether of the enol form of methyl propyl ketone and treatment of the ethyl ether with zinc gave pentene-1.

4. On treatment with alcoholic alkali, ethers of 1-bromopenten-2-ol-4 gave diethers of unsaturated glycols and on reduction over Raney nickel followed by colloidal palladium, they gave ethers of secondary amyl alcohol.

5. As a result of the investigation it was established that alkyl hypobromites, to a greater extent than alkyl hypochlorites, add to piperylene in the 3,4 position; however, in comparison with divinyl, piperylene forms much more of the 1,4-products.

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Leningrad Lensoviet Institute
of Technology

INVESTIGATION IN THE FIELD OF CONJUGATED SYSTEMS

LXV. HYDROGENATION OF VINYLALKYLACETYLENES IN THE PRESENCE OF COLLOIDAL PALLADIUM

Kh. V. Balyan, A. A. Petrov and Yu. I. Porfiryeva

In previous articles of this series it was shown that vinylalkylacetylenes add hydrogen halide to the acetylene bond, while with bromine, hypobromous acid and alkylhypobromites they form addition compounds mainly at the double bond [1-3]. In contrast to **the above homologs**,vinylalkylacetylene adds halogens and hydrogen halides either to the triple bond or in the 1, 4-position, while the fixation of the positively polarized part of the added molecule proceeds in accordance with the acetylene grouping [4, 5].

In the light of this data, study of the catalytic hydrogenation of vinylalkylacetylenes over colloidal palladium, which is known to be among the most selective catalysts with double and triple bonds, seemed to be of great intesest. It was known from the literature data that vinyl- and isopropenylacetylenes added hydrogens to the triple bond in the first place in the presence of colloidal palladium and then the reaction was complicated by subsequent hydrogenation of the initially formed dienes to corresponding olefins [7-9].

Our catalytic hydrogenation experiments with vinylmethyl- and vinylethylacetylenes had analogous results: hydrogen was added mainly to the triple bond with the formation of piperylene and hexadiene-1, 3, which however, under the experimental conditions, was hydrogenated further to a considerable degree, to the corresponding olefins (especially in the case of vinylethylacetylene).

The curve of the uptake rate for vinylmethylacetylene hydrogenation had a break only after the addition of 2 hydrogen molecules. The third hydrogen molecule as was noticed in other cases [10], practically did not add (Curve 1, figure).

Three possible hydrocarbons would be expected from the addition of one hydrogen molecule to vinylmethylacetylene:

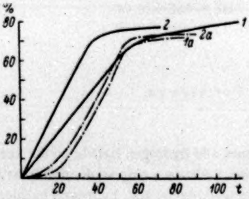
$$CH_3{-}CH{=}CH{-}CH{=}CH_2, \quad CH_3{-}C{\equiv}C{-}CH_2{-}CH_3 \text{ and } CH_3{-}CH{=}C{=}CH{-}CH_3.$$

The hydrogenation products actually obtained (34-35° fraction) after fractional distillation, were treated with excess bromine in chloroform. The bromides were separated into two parts: 1) dibromides, produced from the olefins, and 2) tetrabromides, arising from the diolefins. The amount of dibromides formed decreased and the amount of tetrabromides increased with the increase in boiling point of the fractions. The 46-55° fraction gave no dibromides.

The amylene mixture regenerated from the dibromides by zinc treatment, produced formaldehyde, acetic and propionic acids by ozone cleavage. Thus, it was shown that a mixture of pentene-1 and pentene-2 was obtained from vinylmethylacetylene hydrogenation. A mixture of these hydrocarbons was also obtained during piperylene hydrogenation [11].

Twenty-eight percent of crystalline piperylene tetrabromide with m. p. 114° was separated from the tetrabromides by freezing. It is known from the literature data that cis-piperylene gives 38% of crystalline tetrabromide when brominated while trans-piperylene gives only 13.8% [12]. By comparing this data with our values it may be concluded that vinylmethylacetylene hydrogenation produces mainly cis-piperylene.

A hydrocarbon, with constants similar to those found earlier for piperylene, was regenerated from the liquid tetrabromides. In the combination scattering spectrum of the material, frequencies characteristic for piperylene were detected, in particular one at 1655 cm^{-1} (trans-piperylene frequency) [13], as well as one of the more intense frequencies of the vinylmethylacetylene triple bond (2236 cm^{-1}). Apparently the latter material was present as a slight trace. A characteristic frequency of the methylethylacetylene triple bond (2304 cm^{-1}) was not in the spectrum.



Curves for Rate of Hydrogenation. 1) Vinylmethylacetylene; 1a) the same with p-thiocyanochlorobenzene; 2) vinylethylacetylene; 2a) the same with p-thiocyanochlorobenzene.

To detect the latter material we examined the combination scattering spectrum of the 55-57° fraction, which should have been the richest in methylethylacetylene. In the spectrum of this fraction, besides the frequencies characteristic of cis-piperylene and the parent substance, a weak 2306 cm^{-1} frequency was detected which could be ascribed to methylethylacetylene [14]. However, the amount of this fraction was so small that even if half of it consisted of methylethylacetylene the yield of this hydrocarbon would be less than 2-3%.

The 59-61° fraction was that of unreacted vinylmethylacetylene. This was proved by converting the material into the ketone $CH_3-C\equiv C-CO-CH_3$, using the method described earlier.

We estimated the amylene and piperylene content in the hydrogenation products by the amount of dibromides and tetrabromides produced.

The molar ratio between the amounts of dibromides and tetrabromide obtained from all fractions and calculated for the total fraction weight was 1:1.4 (part of each fraction investigated was brominated). If the 59-61° fraction and half of the 46-59° were considered as being unreacted vinylmethylacetylene, then the composition of the mixture after hydrogenation was approximately as follows: amylene 33%, piperylene 47% and unreacted vinylmethylacetylene 20%.

We also investigated vinylmethylacetylene hydrogenation with a hydrocarbon: H_2 ratio of 1:1.5. In this case the composition of the mixture obtained was approximately: amylene 31.6%, piperylene 56% and vinylmethylacetylene 12.4%.

A catalyst with p-thiocyanochlorobenzene added was also used to increase the selectivity of the hydrogenation process.

One of us has shown in his work [15] that the selectivity of the process noticeably increased when certain acetylene and ethylene alcohols were hydrogenated over palladium in the presence of this material: the hydrogenation rate of the triple bond fell considerably less than that of the double. A decrease in hydrogenation rate, especially at the start of the process (Curve 1a, figure) was observed in experiments with vinylmethylacetylene in the presence of p-thiocyanochlorobenzene, and the reaction products contained a somewhat larger amount of piperylene in comparison to the previous experiment. The ratio amylene : piperylene became approximately equal to 1:2.

The course of the vinylethylacetylene hydrogenation uptake curve did not differ from the one for vinylmethylacetylene (Curve 2, figure). Three hydrocarbons could be expected from the addition of 1 mole of hydrogen to vinylethylacetylene, among which hexadiene-1, 3 (as a cis-and trans-mixture) and diethylacetylene were known.

Di-and tetrabromides in the molar ratio of 1.2:1 were formed on brominating the vinylethylacetylene hydrogenation products (b. p. 57-75°). A mixture of hexenes was regenerated from the dibromides. Formaldehyde and butyric acid were found in the decomposition products of the ozonides, obtained from this mixture. This data indicated the presence of hexene-1 and hexene-2 in the mixture. Frequencies corresponding to all three hexenes were detected in the combination scattering spectrum of the material (Table 9).

About 20% of crystalline hexadiene-1, 3 tetrabromide with m. p. 91.5° was separated from the tetrabromides by freezing. A hydrocarbon, with constants similar to hexadiene-1, 3, was obtained from the liquid tetrabromides. The combination scattering spectrum of the material showed that it consisted of hexadiene-1, 3 with a trace of the original vinylethylacetylene (Table 9).

The composition of the mixture obtained by vinylethylacetylene hydrogenation is approximately as follows: hexene 40%, hexadiene-1,3 35% and vinylethylacetylene 25%. The composition of the hydrogenation products remained practically unchanged when vinylethylacetylene was hydrogenated in the presence of an inhibitor (p-thiocyanochlorobenzene).

Thus, it was established by this investigation that vinylalkylacetylenes, similarly to vinylacetylene, add hydrogen to the triple bond and then the reaction is complicated, especially in the case of vinylethylacetylene, by subsequent hydrogenation of the diolefins formed to olefins. The order of hydrogen addition to vinylalkylacetylenes turned out to be the same as the order of hydrogen halide addition, at least, in the position of initial attack (addition position of the positively polarized hydrogen in the case of the hydrogen halides).

EXPERIMENTAL

Hydrogenation of Vinylmethylacetylene

For the investigation we used vinylmethylacetylene with b. p. 55-59.5°, d_4^{20} 0.7396, n_D^{20} 1.4480, which corresponds to the literature data [16].

a) The results of one of the five experiments, demonstrating the character of the hydrogenation process, are given in summary form in Table 1 and as Curve 1 in the graph. From these data can be seen that about 640 ml of H_2, an amount corresponding to approximately 2 hydrogen molecules per hydrocarbon molecule, were quite rapidly absorbed at the beginning of hydrogenation and that then the rate of the process sharply decreased.

TABLE 1

0.865 g Vinylmethylacetylene, 30 ml CH_3OH, 1 ml Colloidal Pd (1 mg Pd), 22°, 770 mm. Theoretical Amount of H_2 Calculated for 3 H_2 Molecules Per Hydrocarbon Molecule – 939.4 ml.

Time (in minutes)	12	24	36	48	60	72	123
v	125	266	411	545	653	686	773
H_2 (%)	13.3	28.3	43.7	58.1	69.5	73	82.3

b) Three hydrogenation experiments using larger portions of hydrocarbons, with a ratio of 1 hydrogen molecule per 1 hydrocarbon molecule, were also carried out. We used 250 ml of methanol and 30 ml of catalyst for each experiment. The experimental conditions and the yield in hydrogenation products are given in Table 2.

TABLE 2

Experiment number	Portion (in g)	Pressure (in mm)	Temperature	Volume of absorbed H_2 (in liters)	Duration of experiment (in min)	Yield (in %)
1	22.65	771.6	20°	8.12	90	94.2
2	25.74	765.7	23	9.55	100	89.1
3	20.72	756.5	21	7.54	80	92.7

After the end of hydrogenation the reaction mixtures was diluted with water and the hydrocarbons distilled in a fractionating column until the distillate lost the turbidity caused by water. The distillate was saturated with $CaCl_2$. The hydrocarbon layer was separated, washed with a saturated $CaCl_2$ solution and dried over fused $CaCl_2$. All the hydrocarbon operations were carried out in a well cooled system.

The products of the three experiments were combined and distilled in a Widmer fractionating column (50 cm). The results of the distillation of 64.1 g of hydrogenation products are given in Table 3, constants of possible hydrocarbon hydrogenation products are in Table 4.

To detect methylethylacetylene, the combination scattering spectrum of the 55-57° fraction was taken. The data are given in Table 5.

Fifty-eight grams of bromine was added to a solution of 15 g of the 1st, 2nd and 3rd fractions (34-40°), taken in amounts proportional to their weight, in 100 ml of chloroform with ice and salt cooling of the mixture. After the mixture stood overnight, the bromine excess was removed by a sulfite solution and the chloroform distilled, 7 g of crystalline piperylene tetrabromide was separated by freezing. The residue of 49 g was distilled in vacuum at 7 mm. The following fractions were obtained: 1st (59-60°), 26 g; 2nd (135-140°) 18 g; residue 2 g.

By brominating 12.5 g of the 4th, 5th and 6th fractions (40-46°) under the same conditions with chloroform solution of 60 g bromine, 15.6 g of crystalline piperylene tetrabromide was separated directly from the reaction mixture (after chloroform distillation). By distilling the residue (60 g) in vacuum at 7 mm the following fractions were obtained: 1st (to 60°), 8.6 g; 2nd (130-140°) 35.9 g; residue 1.1 g. An additional 4 g of solid tetrabromide was separated from the 2 nd fraction by freezing.

TABLE 3

Fraction number	Boiling range	Weight (in g)	d_4^{20}	n_D^{20}
1	34—36°	17.2	0.6507	1.3921
2	36—38	3.5	0.6596	1.3980
3	38—40	6.4	0.6659	1.4060
4	40—42	5.7	0.6735	1.4173
5	42—44	5.2	0.6827	1.4260
6	44—46	3.4	0.6898	1.4330
7	46—49	3.3	0.6971	1.4400
8	49—52	2.2	0.7055	1.4400
9	52—55	1.6	0.7135	1.4412
10	55—57	3.5	0.7258	1.4438
11	57—59	2.8	0.7310	1.4456
12	59—61	5.2	0.7398	1.4480
13	Residue	2.1	—	—

TABLE 4

Hydrocarbon	Boiling point	d_4^{20}	n_D^{20}	Characteristic frequency in the combination scattering spectrum (cm^{-1})
$CH_3-CH=CH-CH=CH_2$ (cis)	44.1°	0.6910	1.4363 [11]	1646 [13]
$CH_3-CH=CH-CH=CH_2$ (trans)	42.0	0.6760	1.4301	1655
$CH_3-C\equiv C-C_2H_5$	56	0.687	1.4004 [17]	2238,2304 [14]
$CH_3-CH=C=CH-CH_3$ . . .	48.3	0.6950	1.4284 [17]	1070,1140 [14]

21.5 g of tetrabromides was obtained by brominating the 46-55° fractions (6.1 g) under the usual conditions (30 g bromine). There were no dibromides. 5.5 g of solid piperylene tetrabromide was separated from the tetrabromides. In all, 34.6 g dibromides, 65.9 g liquid tetrabromides and 32.1 g solid piperylene tetrabromide (28%) were obtained from the bromination of 33.6 g of hydrocarbons.

The dibromides obtained from different fractions were combined and redistilled at 20 mm.

B. p. 73.5-74° (20 mm) (80% of all the amount), d_4^{20} 1.6766, n_D^{20} 1.5085. Found %: Br 69.56. $C_5H_{10}Br_2$. Calculated %: Br 69.49.

The following constants are given in the literature for the two dibromides possible in this case [18]: 1, 2-dibromopentane, b. p. 68° (12 mm), d^{19} 1.668, n_D^{21} 1.5088; 2, 3-dibromopentane, b. p. 69-70° (17 mm), d_0^{14} 1.6863, n_D^{20} 1.5098.

5.4 g (84%) of hydrocarbons was regenerated from the dibromides (21 g) by zinc in an aqueous-alcohol solution.

B. p. 34.8-35.8°, d_4^{20} 0.6500, n_D^{20} 1.3798.

The following constants are given in the literature for isomeric pentenes [17]: pentene-1, b. p. 30.0°, d_4^{20} 0.6405, n_D^{20} 1.3715; pentene-2, b. p. 36.3-36.8°, d_4^{20} 0.6505, n_D^{20} 1.3797.

TABLE 5*

55-57° Fraction	Piperylene, from liquid tetrabromide	Literature Data			
		Piperylene, from liquid tetrabromide [13]	Methylethyl-acetylene [14]	Dimethyl-allene [14]	Dimethyl-acetylene
–	896(5b)	897(4)	–	–	–
913(5d)	–	–	–	–	918(3d)
959(1d)	958(1b)	955(1)	954(3)	–	–
1026(5)	1033(3)	1032(1)	–	1026(1)	1032(3d)
1060(1)	–	–	1063(4)	1070(5)	–
–	–	–	–	1140(6)	–
1162(10)	1167(2)	1174(3)	–	–	1166(6)
–	1182(10)	1183(7)	–	–	–
1246(10)	1248(5)	1250(8)	–	–	–
1289(12)	1291(10)	1292(10)	–	–	1291(10)
1376(8)	1378(7)	1376(6)	1380(5)	1352(1/2)	1377(6)
1411(10)	1413(7)	1413(5)	–	–	1409(8)
–	–	1432(3)	–	–	–
1444(2b)	1450(7)	1451(6)	1447(4v)	1464(3)	–
1589(5)	–	1596(4)	–	–	1589(2)
1606(12)	–	1603(4)	–	–	1606(12)
1645(8)	–	1646(10)	–	–	–
–	1655(10)	1655(10)	–	–	–
2094(2)	–	–	–	–	2094(1)
2236(15)	2236(4)	–	2238(5)	–	2235(20)
2306(1)	–	–	2304(3)	–	–
2336(8)	–	–	–	–	2336(4)
–	–	–	–	2719(1)	–
2861	–	2860(3)	2861(3)	2861(1)	–
–	2887(2)	–	–	–	2887(2)
2922(12)	2922(8)	2921(6)	2922(5)	2913(8b)	2917(12)

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*Only the middle range of the spectrum was used in all cases. The authors thank V. A. Kolesova for the spectral investigations.

3.8 g of hydrocarbon was ozonized. The ozonide was decomposed in a 20% potassium iodide solution and acidified with acetic acid. The iodine separated was titrated off with hyposulfite. The mixture was then heated with a 2% β-naphthol solution. The precipitate was filtered off, washed with hot water, dried at 40° and weighed. 0.0873 g of dinaphthomethane was obtained with b. p. 189-191° [19]. The remaining ozonization products (aldehydes) were oxidized with permanganate until decolorization ceased. Two grams of acids with a boiling range of 120-140° were extracted with ether from the solution obtained. Propionic acid in the form of a basic lead salt [20] was isolated from this mixture. Its silver salt was analyzed.

Found %: Ag 59.68. $C_3H_5O_2Ag$. Calculated %: Ag 59.62.

The combined liquid tetrabromides (61 g) were redistilled at 10 mm. The following fractions were obtained: 1st (up to 140°) 2 g; 2nd (140-145°) 42.7 g; 3rd (145-155°) 7.8 g; residue 4 g.

For the fraction 140-145° (10mm), d_4^{20} 2.3596, n_D^{20} 1.5990.

Found %: Br 81.77. $C_5H_8Br_4$. Calculated %: Br 82.43.

The following constants are given in the literature for liquid piperylene tetrabromide [21]: b. p. 121-132° (3 mm), d_4^{20} 2.3195, n_D^{20} 1.5915.

The solid tetrabromide was recrystallized from methyl alcohol and identified by mixed melting point with known piperylene tetrabromide with a m. p. 114°.

A hydrocarbon was regenerated from the liquid tetrabromides (50.5 g) by zinc. Yield 7.5 g (85%):

B. p. 41-44.5°, d_4^{20} 0.6867-0.6881, n_D^{20} 1.4322-1.4338.

The combination scattering spectrum of this material is given in Table 5. The literature data for cis- and trans-piperylenes is given in Table 4.

The quantities of di- and tetrabromides obtained were converted to the total weight of the corresponding fractions. 57.2 g of dibromides and 132.5 g of tetrabromides should have been produced, which gives a molar ratio of amylenes to piperylene of 1:1.4.

8.0 g of benzosulfodibromoamide was added to 3.3 g of the 59.0-61° fraction in 25 ml methanol. 5.3 g of bromoether with b. p. 64-66° (10 mm), n_D^{20} 1.4882, was separated from the reaction mixture by the usual method. By heating the bromoether with alcoholic alkali the enol ether $CH_3-C\equiv C-C(OCH_3)=CH_2$ with b. p. 38-40° (20 mm), n_D^{20} 1.4480 was obtained. The constants of the bromoether and of the latter material differ little from those found earlier for them [1].

The enol ether was dissolved in 5% H_2SO_4 and a ketone was distilled, together with water, from the solution: the ketone formed a 2, 4-dinitrophenylhydrazone, with m. p. 148°, characteristic of pentyn-3-one-2 by the action of 2, 4-dinitrophenylhydrazine in acetic acid (from alcohol) [1].

c) 0.8445 g of hydrocarbon, 30 ml methanol, 1 mg of catalyst and 0.4 mg of p-thiocyanochlorobenzene were used for studying the character of vinylmethylacetylene hydrogenation in the presence of an inhibitor. Allowing 3 hydrogen molecules for one hydrocarbon molecule, 917.1 ml H_2 would be used under the experimental conditions (22°, 770 mm). The experimental data are given as Curve 1a in the graph.

d) 30.9 g of hydrocarbon, 200 ml methanol, 30 mg and 10 mg of p-thiocyanochlorobenzene were used for investigating the hydrogenation products in the presence of an inhibitor. Allowing 1 hydrogen molecule for 1 hydrocarbon molecule, 11.3 g of H_2 would be used under the experimental conditions (20°, 759 mm). The hydrogenation lasted for 2 hours 15 minutes. Reaction product yield 28 g (91%). Fractions similar to those given in Table 3 were obtained by distilling 24 g of the material.

Fractions within the boiling range of 36-54° were brominated in chloroform. 12.2 g of dibromides and 44 g of tetrabromides were obtained of which 17 g (38.6%) was crystalline piperylene tetrabromide. These data show that the reaction mixture contained amylenes and piperylene in a ratio of 1:2.

e) A portion of hydrocarbons (19.27 g) was hydrogenated in 200 ml of CH_3OH in the presence of 30 mg colloidal Pd and 8 mg of p-thiocyanochlorobenzene till absorption of 11.08 liters of H_2, which corresponded to 1.5 hydrogen molecules for each hydrocarbon molecule. 17.1 g of hydrogenation products were obtained. 13 g of the material was distilled at 36-44°. 11.6 g of dibromides and 29 g of tetrabromides (11.5 g of crystalline tetrabromide) were obtained by brominating 12.8 g of hydrocarbons in chloroform. These figures (considering that the residue consisted of equal amounts of piperylene and vinylmethylacetylene) give a ratio for amylenes and piperylene of 1 : 1.8.

Hydrogenation of Vinylethylacetylene

The vinylethylacetylene had the constants: b. p. 83.5-84°, d_4^{20} 0.7479, n_D^{20} 1.4522, which corresponds with the literature data [16].

a) The results of one of the experiments, demonstrating the character of the hydrogenation process, are given in summary form in Table 6 and as Curve 2 in the graph. Here also the hydrogenation rate decreased after the absorption of approximately 2 hydrogen molecules for each hydrocarbon molecule.

TABLE 6

1.2023 g Vinylethylacetylene, 30 ml CH_3OH, 1 ml Colloidal Pd (1 mg Pd), 22°, 770 mm. Theoretical Amount of H_2 Calculated for 3 Hydrogen Molecules per Hydrocarbon Molecule – 1077.0 ml

Time (in min)	12	24	36	48	60	72
v	238	496	751	800	819	828
H_2 (in %)	22.1	46.1	69.7	74.3	76.1	76.9

b) 84.7 g of hydrocarbons (in three portions) was used in the reactions for the investigation of the hydrogenation products. 24.48 liters of H_2 was absorbed (approximately 1 molecule per hydrocarbon molecule). As a result of the hydrogenation 82.7 g (95%) of hydrogenation products were obtained. The results of the distillation of this mixture are given in Table 7, the constants of possible hydrogenation products are given in Table 8.

TABLE 7

Fraction	Boiling point	Weight (in g)	d_4^{20}	n_D^{20}
1	57—64°	2.5	0.8577	1.4041
2	64—70	29.7	0.6919	1.4068
3	70—75	10.8	0.6951	1.4272
4	75—78	4.2	0.7225	1.4400
5	78—82	9.1	0.7387	1.4458
Residue	—	14.4	—	—

TABLE 8

Material	Boiling point	d_4^{20}	n_D^{20}
$C_2H_5—CH{=}CH—CH{=}CH_2$	72—74°	0.7140	1.4416 [21]
$C_2H_5—C{\equiv}C—C_2H_5$	80—80.5	0.7230	1.4220 [47]

The first three fractions were brominated with excess bromine in chloroform. 58 g of dibromides (b.p. 80-90° at 16 mm) and 79 g of tetrabromides (b.p. higher than 130° at 10 mm) were obtained on distillation.

Repeated distillation of the dibromides at 16 mm gave the fractions: 1st (to 83°) 3.7 g (d_4^{20} 1.5860, n_D^{20} 1.5028); 2nd (83-85°) 36.3 g (d_4^{20} 1.5920, n_D^{20} 1.5032); 3rd (85-87°) 14.3 g (d_4^{20} 1.5930, n_D^{20} 1.5032); residue 1.7 g.

For the 83-85° fractions (16 mm) found %: Br 66.02, 66.04. $C_6H_{12}Br_2$. Calculated %: Br 65.51

Hydrocarbon was regenerated from the first three fractions of dibromide. B. p. 65-65.5° (10.9 g), d_4^{20} 0.6790, n_D^{20} 1.3918. The lower and higher fractions were only 1 g.

The following constants are given in the literature for various hexenes [17]: hexene-1, b.p. 63.5°, d_4^{20} 0.6732, n_D^{20} 1.3879; hexene-2 (cis), b.p. 68.2° (749 mm), d_4^{20} 0.6845, n_D^{20} 1.3954; hexene-2 (trans), b.p. 67.5° (750 mm), d_4^{20} 0.6780, n_D^{20} 1.3935; hexene-3 (cis), b. p. 66.8°, d_4^{20} 0.6796, n_D^{20} 1.3934; hexene-3 (trans), b. p. 67.5° (745 mm), d_4^{20} 0.6779, n_D^{20} 1.3938.

The hexene mixture obtained by us was ozonized (5.5 g). Formaldehyde was detected in a separate sample of ozonide by the method described earlier (0.1703 g of dinaphthomethane was obtained from 0.4956 g of ozonide). The rest of the ozonide was converted into acids. The acids boiled in the temperature range of 130-160°. Butyric acid was found qualitatively in the acid mixture by testing with hydrogen peroxide and Mohr's salt [22].

TABLE 9

Hydrocarbon	Characteristic frequencies of multiple bonds in combination scattering spectra (cm^{-1})	
	double bond	triple bond
Hexene from Dibromides	1640(2)	–
	1652(8)	
	1670(2)	
Hexene-1 [23]	1649	–
Hexene-2 (cis) [23]	1666	–
Hexene-2 (trans) [23]	1681	–
Hexene-3 (cis) [23]	1656	–
Hexadiene from liquid tetrabromide	1642(4)	2100(1)
	1657(15)	2192(3)
	–	2227(10)
	–	2330(d1)
Hexadiene-1,3 (cis-trans) [23]	1660	–
Vinylethylacetylene (hexen-1-yne-3)	1606(15)	2092(d1)
	–	2196(4)
	–	2230(20)
	–	2330(4)
Diethylacetylene [24] (hexene-3)	–	2229(10)
	–	2248(8)
	–	2300(7)

The combination scattering spectrum of hydrocarbon was taken. It can be seen from Table 9 that all three possible hexenes are found in the mixture.

Repeated distillation of tetrabromides at 5 mm gave the following fractions: 1st (up to 135°) 4.3 g; 2nd (135-145°) 12.8 g; 3rd (145-149°) 37.0 g; 4th (149-160°) 5.5 g; residue 5.0 g.

7.2 g and 4.5 g of crystalline tetrabromide was separated by cooling from the 3rd and 4th fractions respectively.

For the liquid tetrabromide after separation of crystals:

B. p. 143-144° (5 mm), d_4^{20} 2.2338, n_D^{20} 1.5912.

Found %: Br 78.54, 78.23. $C_6H_{10}Br_4$. Calculated %: Br 79.56

Crystalline tetrabromide melts at 91-91.5° (from methanol).

Found %: Br 82.01. $C_6H_{10}Br_4$. Calculated %: Br 79.56.

The same melting point was given in the literature for crystalline tetrabromide hexene-1, 3 [21].

8.5 g (96.6%) of hydrocarbon with b. p. 74-76°, d_4^{20} 0.7172, n_D^{20} 1.4429 was regenerated from liquid tetrabromide (43 grams). The combination scattering spectrum of the material is given in Table 9, from which it can be seen that the material is hexadiene-3 with a trace of vinylethylacetylene.

The ratio of the di- and tetrabromide quantities obtained gives the ratio 1.2 : 1 for the hexenes and hexadienes in the hydrogenation products.

c) 9.05 liters H_2 (calculated for 1 hydrogen molecule per 1 hydrocarbon molecule) was absorbed in the hydrogenation of 30.6 g of vinylethylacetylene in the presence of 30 mg colloidal Pd and 4 g of inhibitor (p-thiocyanochlorobenzene) at 19° and 769.5 mm. The same fractions as in the preceding experiment were obtained by distilling 19.8 g (94%) of the materials on a fractionating column.

15.5 g of dibromides and 20.5 g of tetrabromides were formed by brominating 11.1 g of the fractions boiling in the temperature range of 66-75°. From the latter 6.1 g of crystalline tetrabromide with m. p. 91-91.5° was separated by freezing. Thus, in this case the ratio of hexenes to hexadiene was 1.2 : 1 in the hydrogenation products.

d) A portion of 1.0343 g of hydrocarbon was taken for determining the hydrogenation rate of vinylethylacetylene in the presence of an inhibitor. The experimental conditions were the same as for vinylmethylacetylene. The experimental results are given in Curve 2a in the graph.

SUMMARY

1. It was shown that in vinylmethyl- and vinylethylacetylene hydrogenation in the presence of colloidal palladium, hydrogen adds to the triple bond, while at the same time further hydrogenation of the dienes-1, 3 formed to olefins occurs. This last process is especially marked in the case of vinylethylacetylene.

2. It was established that in the case of vinylethylacetylene the addition of an inhibitor increases the selectivity of the hydrogenation process.

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Leningrad Lensoviet Institute of Technology.

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CATALYTIC ALKYLATION OF CHLOROBENZENE BY PROPYL ALCOHOLS

M. B. Turova-Polyak, N. V. Danilova and N. V. Kuklina

The alkylation of chlorobenzene is at present carried out mainly in the liquid phase by alcohols, halide derivatives or olefins in the presence of phosphoric acid [1], sulfuric acid [2] or hydrofluoric acid [3]. Aluminum chloride appears to be the best catalyst for liquid phase alkylation of chlorobenzene [4-7]. In their paper [8] Yu. G. Mamedalieva and Sh. V. Valieva show the possiblity of catalytic alkylation of chlorobenzene in the vapor phase but at increased pressure; the propylene-propane fraction of pyrolysis gases served as the alkylating agent.

We alkylated benzene by alcohols in the gas phase with an aluminosilicate catalyst and at atmospheric pressure [9, 10]. The best alkylbenzene yields were obtained by using propyl alcohols. In the present work the alkylation of chlorobenzene by propyl alcohols was carried out in a circulating system over an aluminosilicate cracking catalyst and at atmospheric pressure. An increase in the chlorobenzene concentration in the reaction mixture from 2 to 22 molecules per alcohol molecule helped to raise the isopropylchlorobenzene yield, mainly p-isomer, from 19.5 to 97% on alcohol in the reaction.

Chlorobenzene alkylation by either isopropyl or n-propyl alcohol produced isopropylchlorobenzene. However, the use of normal alcohol for alkylation lowered the yield of monoisopropylchlorobenzene to 55%. The formation of a reaction product with the same structure was explained, in our opinion, by the formation of propylene during the process and the addition of the aromatic compound to it.

The composition and yield of the alkylation products depended on whether pure chlorobenzene or the excess, distilled off from previous alkylation experiments, was used for the alkylation. In the former case, besides the monoisopropylchlorobenzene, a small amount of polyalkylchlorobenzene was formed; in the latter the yield of polyisopropylchlorobenzene fell and that of monoisopropylchlorobenzene rose: in alkylation with isopropyl alcohol, in optimal conditions, from 64 to 97%; in alkylation with n-propyl alcohol from 55.1 to 68.3%.

This phenomenon may be explained by the presence of insignificant amounts of unsaturated compounds in the chlorobenzene distilled off from previous experiments, and these acted in this case as specific catalysts. If the low-boiling fraction (83-135°, Table 3) was distilled off from the used chlorobenzene and the latter was then subjected to alkylation, the same results were obtained as those for pure chlorobenzene.

Comparison of results of previous and the present work shows that in benzene alkylation by isopropyl alcohol (component ratio 4 : 1, temperature 325°, volume rate 0.2) the yield of isopropylbenzene was 45%; in chlorobenzene alkylation by isopropyl alcohol, under similar conditions, the yield of isopropylchlorobenzene was only 25.4%. This data indicates that the presence of chlorine in the benzene ring passivates the alkylation reaction, and is in full agreement with the available data on the effect of halides on substitution reaction.

EXPERIMENTAL

The experiments were carried out on apparatus described earlier [9]. An industrial aluminosilicate cracking catalyst was used; after the experiment it was regenerated by dry air for 2.5-3 hours at 500°, after which its activity was restored. Each experiment was carried out with an equal quantity of reaction mixture. After the end of the experiment the catalyzate residue was removed by a slow current of nitrogen for 15 minutes, and then the reaction product was dried and fractionated.

There were no changes in the chlorobenzene when passed over the catalyst with a volume rate of 0.2 at 250°. Isopropyl alcohol under these same conditions was dehydrated to 96-97%; the gas thus evolved was

99.0-99.5% propylene. Besides water in the liquid catalyzate there was a layer of unsaturated hydrocarbons corresponding to 3-4% of the alcohol in the reaction which was, apparently, a condensation product of propylene and had b. p. 69-200° and n_D^{20} 1.4000-1.4920.

The effect of temperature reaction mixture composition and chlorobenzene quality on the monoisopropylchlorobenzene yield. Isopropyl alcohol, pure chlorobenzene (I) as well as chlorobenzene (II), distilled from previous experiments (fraction 83-137°, Table 3) and containing a minute quantity of unsaturated material with b. p. up to 135°, were used in these experiments.

It can be seen from the data in Table 1 that 250° is the optimum temperature for ratios of chlorobenzene : isopropyl alcohol from 2 : 1 to 6 : 1. The reactions with different ratios of components were carried out only at a temperature of 250°, which was the optimum in all cases.

TABLE 1

Monoisopropylchlorobenzene Yield on Alkylation of Chlorobenzene by Isopropyl Alcohol (in wt. % at a volume rate 0.2)

Temperature of Expt.	Molar Ratio Chlorobenzene : Isopropyl Alcohol													
	2 : 1		4 : 1		6 : 1		8 : 1		14 : 1		20 : 1		22 : 1	
	chlorobenzene		chlorobenzene		chlorobenzene		chlorobenzene		chlorobenzene		chlorobenzene		chlorobenzene	
	(I)	(II)	(I)	(II)	(I)	(II)	(I)	(II)	(I)	(II)	(I)	(II)	(I)	(II)
225°	11.1	–	28.4	–	30.25	–	–	–	–	–	–	–	–	–
250	16.3	19.5	31.0	37.0	33.4	39.2	40.3	56.0	45.0	76.0	63.4	94.3	64.0	97.0
275	15.6	–	28.1	–	30.4	–	–	–	–	–	–	–	–	–
300	15.1	–	27.4	–	29.3	–	–	–	–	–	–	–	–	–
325	12.7	–	25.4	–	–									

The same effects were observed on alkylation of chlorobenzene by n-propyl alcohol (Table 2).

The effect of the rate of introduction of the reaction mixture. The experiments were carried out with a mixture of chlorobenzene: isopropyl alcohol, ratio of 4 : 1 at 250°. The volume rate was varied from 0.1 to 1.8. The results, given in the diagram, for this series of experiments show that the greatest yield of isopropylchlorobenzene was obtained at a volume rate of 0.2.

Investigation of reaction products. The results of the distillation of the catalyzate obtained on chlorobenzene alkylation by iso- and n-propyl alcohols at 250° and with a molar ratio of the components of 4 : 1 are given in Table 3. Analogous results were obtained by distilling alkylation products of experiments using mixtures containing 14 moles chlorobenzene per 1 mole alcohol.

TABLE 2

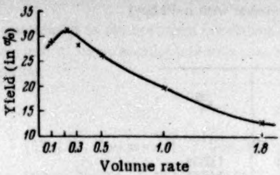
Monoisopropylchlorobenzene Yield on Alkylation of Chlorobenzene by n-Propyl Alcohol (in wt. % at a volume rate 0.2)

Temperature of experiment	Molar ratio chlorobenzene: n-propyl alcohol			
	4 : 1		22 : 1	
	chlorobenzene		chlorobenzene	
	(I)	(II)	(I)	(II)
225°	22.6	—	—	—
250	25.5	30.0	55.1	68.3
275	25.0	—	—	—
300	21.2	—	—	—
325	20.6	—	—	—

The alkylation products distilled in the temperature range 190-205° at a higher content of chlorobenzene in the mixtures and consequently they did not contain any polysubstituted chlorobenzene.

The combined fractions 190-206° and 206-230° were distilled in vacuum in a bubble-cap fractionating column of 40 theoretical plates. The distillation results are given in Tables 4 and 5.

The constants for the main fractions isolated by us and literature data on o- and p-isopropylchlorobenzene (there is no data on m-isomer) are given in Table 6.



The effect of volume rate on isopropylchlorobenzene yield.

We did not investigate the higher fractions of polyisopropylchlorobenzenes (77.5-107°, Table 4 and 74.7-105.0°, Table 5).

TABLE 3

Results of the Catalyzate Distillation

Boiling point of fraction (760 mm)	Amount of fraction in the catalyzate on alkylation (in wt. %)		n_D^{20}	d_4^{20}
	by isopropyl alcohol	by n-propyl alcohol		
83—135° .	3.50	2.1	1.5186	1.0653
135—137* .	82.10	83.5	1.5245	1.1005
137—190 . .	0.90	0.7	1.5230	1.0862
190—206 **	8.42	7.5	1.5140	1.0193
206—230 ***	2.28	2.0	1.5120	0.9954
Residue	1.00	2.2	—	—
Losses	1.80	2.0		

*Excess chlorobenzene.

**Main alkylation product; see Table 6 for the constants of isopropylchlorobenzenes.

***Polyisopropylchlorobenzenes were contained in the fraction.

TABLE 4

Distillation of Alkylation Products of Chlorobenzene with Isopropyl Alcohol

Fraction number	Boiling point (10 mm)	Yield (in vol. %)	n_D^{20}	d_4^{20}
I	70.5— 72.5°	2.7	1.5192	1.0376
II	72.5— 73.5	6.2	1.5170	1.0338
III	73.5— 76.0	6.5	1.5157	1.0284
IV	76.0— 77.5	47.9	1.5130	1.0223
V	77.5— 80.5	2.7	1.5124	1.0180
VI	80.5—107.0	21.0	1.5106	0.9893
Residue and losses	—	13.0	—	—

TABLE 5

Distillation of Alkylation Products of Chlorobenzene with n-Propyl Alcohol

Fraction number	Boiling point of the fraction (10 mm)	Yield (in vol. %)	n_D^{20}	d_4^{20}
I	67.0— 68.5	18.5	1.5170	1.0338
II	68.5— 72.5	2.9	1.5141	1.0275
III	72.5— 74.7	39.5	1.5129	1.0221
IV	74.7— 87.0	6.2	1.5111	1.0103
V	87.0—105.0	20.1	1.5100	0.9626
Residue and losses	—	12.8	—	—

To determine the structure of monoisopropylchlorobenzene, some of the fractions were oxidized with nitric acid, d 1.2 [13]. An acid was obtained from the fractions 72.5-73.5° (12 mm) and 67.0-68.5° (10 mm) which after repeated crystallization and sublimation gave crystals with m. p. 143° and 230°. By oxidizing the fractions 76.0-77.5° (12 mm) and 72.5-74.7° (10 mm) and after recrystallization from alcohol and sublimation, an acid with m. p. 241-242° was obtained.

According to the literature data, p-chlorobenzoic acid melts at 242-243° [14], o-chlorobenzoic acid — 141-142° [15] and m-chlorobenzoic acid 158° [16].

Thus, on the basis of distillation and oxidation results, p-isopropylchlorobenzene may be considered as the main alkylation product of chlorobenzene with propyl and isopropyl alcohols.

TABLE 6

Isopropylchlorobenzene Properties

Boiling point of the fraction and of individual compounds	n_D^{20}	d_4^{20}
67.0—68.5° (10 mm) . . 72.5—73.5° (12 mm) . . 189.0—190.5° (760 mm) .	1.5170	1.0338
o-Isopropylchlorobenzene [11] 191.08°	1.5167	1.0341
72.5—74.7° (10 mm) . . 76 —77.5° (12 mm) . 193—194.5° (760 mm) .	1.5130	1.0223
p-Isopropylchlorobenzene 198.3° [11]	1.5117	1.0207
195—197° [4]	1.5140	d_{20}^{20} 1.0022
79— 81° (15 mm) [12]	1.5158	1.0411

SUMMARY

1. The alkylation of chlorobenzene by propyl alcohols was carried out in a circulating system, over an aluminosilicate catalyst and at atmospheric pressure.

2. 250°, a molar ratio of chlorobenzene : isopropyl alcohol equal to 22 : 1 and a volume rate of 0.2 should

be considered as the optimum conditions for obtaining monoisopropylchlorobenzene (in the main para-isomer). The yield of monoisopropylchlorobenzene under these conditions reaches 97% when alcohol is added to the reaction.

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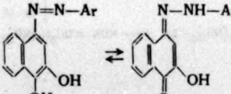
OXIDATION AND OXIDATIVE-HYDROLYSIS OF ORGANIC MOLECULES

XXVIII. OXIDATIVE-HYDROLYSIS OF NITROSUBSTITUTED HYDROXYAZO DYES

O. M. Shemyakina, B. M. Bogoslovsky and M. M. Shemyakin

In one of the previous reports [1] we showed that 1-benzeneazo-3, 4-dihydroxynaphthalene (I; Ar = C_6H_5) was readilyhydrolyzed to a large extent, as a result of its tendency to convert into the tautomeric quinoid form (II; Ar = C_6H_5). The latter is a hydroxynaphthaquinone phenylhydrazone, subject to attack by hydrolyzing agents at the double bond $>C{=}N-$, and the phenylhydrazine and the hydroxynaphthaquinone thus formed undergo a series of further changes



(I) (II)

From this data it seemed possible to achieve a higher stability of such azo dyes to hydrolyzing reagents, by lowering their tendency to convert into the quinoid form (II).

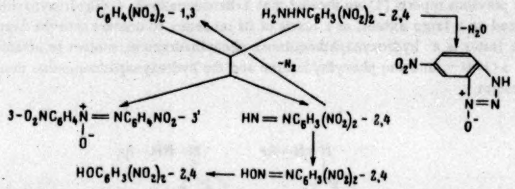
From our point of view it was necessary to introduce into the diazo component of the dye a strong electron-accepting substutuent in the ortho- and para-positions to the azo group so as to decrease the electron density of that nitrogen atom of the azo group with which a hydrogen atom must combine for the formation of the quinoid form. We synthesized two dinitro-substituted hydroxyazo dyes [I; Ar = $C_6H_3(NO_2)_2$-3,5 and $C_6H_3(NO_2)_2$-2,4] to test this hypothesis and studied their behavior with hydrolyzing reagents under the same conditions as in the case of 1-benzeneazo-3,4-dihydroxynaphthalene (I; Ar = C_6H_5). As expected, similarly to the latter, the 3, 5-dinitroazo dye underwent deep changes on heating in a nitrogen atmosphere in an aqueous buffer solution with a pH near 9 (compare [1]), while the 2, 4-dinitroazo dye remained practically unchanged and was only converted into an insoluble sodium salt. Breakdown occurred only under considerably more drastic conditions of prolonged boiling with 1% aqueous caustic soda solution.

It should be noted that in contrast to 1-benzeneazo-3, 4-dihydroxynaphthalene, when boiled in aqueous alkaline solutions both dinitroazo dyes investigated by us underwent not only hydrolysis but oxidative-hydrolysis, as under these conditions, the nitrogroups showed their oxidizing properties. Although the 3, 5-dinitroazo dye started to change under comparatively mild conditions, it underwent very deep oxidative-hydrolysis, accompanied by condensation and resinification of the reaction products; therefore, of the individual materials, only phthalic acid could be isolated in a pure form. The 2,4-dinitroazo dye reacted in an essentially different way. Although it changed only under much more drastic conditions, its reaction was accompanied by less resinification and it was possible, in this case, to isolate several cleavage products, of both azo- and diazo components of the dye — phthalonic and phthalic acids, 2, 4-dinitrophenol and 5-nitro-1, 2, 3-benztriazole.

It was very clear that the initial step of the original 2, 4-dinitroazo dye conversion in these compounds was the hydrolysis of its tautomeric quinoid form [II; Ar = $C_6H_3(NO_2)_2$-2,4] to 2-hydroxy-1, 4-naphthaquinone and

2, 4-dinitrophenylhydrazine. Under the conditions of the reaction (boiling with 1% NaOH) the first of these substances must immediately have undergone hydrolytic cleavage to o-acetylphenylglyoxalic acid, which in its turn was readily oxidized to phthalonic and phthalic acids [1, 2]; therefore quite naturally only these two acids were isolated as cleavage products of the azo compounds of the dye. Although there is some mention in the literature [3] of the problem of further reaction of 2, 4-dinitrophenylhydrazine, formed from the diazo component of the dye, it was not at all clear and therefore we investigated it further.

It was established (see Experimental section) that when 2, 4-dinitrophenylhydrazine was boiled in an inert gas atmosphere with 1% aqueous NaOH solution, it evolved a considerable amount of nitrogen and was converted into the following compounds: 3-oxide of 5-nitro-1, 2, 3-benztriazole (15%), 1, 3-dinitrobenzene (5%), 3, 3'-dinitroazoxybenzene (60%) and 2,4-dinitrophenol (1%) and neither ammonia nor hydrazine was found among the reaction products. The formation reaction of the 3-oxide of 5-nitro-1,2,3-benztriazole was quite obvious from the course of the formation of these compounds; it arose from intermolecular dehydration of the original 2,4-dinitrophenylhydrazine (Figure 1).


$C_6H_4(NO_2)_2$ - 1,3
$H_2NHNC_6H_3(NO_2)_2$ - 2,4
$-H_2O$
$-N_2$
O_2N
NH
N=N
O⁻
3-$O_2NC_6H_4\overset{+}{N}$=$NC_6H_4NO_2$- 3'
O⁻
HN=$NC_6H_3(NO_2)_2$ - 2,4
$HOC_6H_3(NO_2)_2$- 2,4
HON=$NC_6H_3(NO_2)_2$- 2,4

The course of conversion of the latter into 1, 3-dinitrobenzene was sufficiently obvious as it is known (see for example [4]), that arylhydrazines are readily converted by oxidizing agents into aryldiimines, which are immediately decomposed into nitrogen and corresponding hydrocarbons. The 3-oxide of 5-nitro-1, 2, 3-benztriazole may at first have acted as an oxidizing agent, but without doubt, its oxidizing function was later taken over by the 1, 3-dinitrobenzene produced. By reacting with 2, 4-dinitrophenylhydrazine this was reduced to 3, 3'-dinitroazoxybenzene and simultaneously it oxidized the arylhydrazine to 2, 4-dinitrophenyldiimine which was immediately decomposed with the formation again of 1, 3-dinitrobenzene. By this method an interesting process arose in which the reduced oxidizing agent was again regenerated as a result of an oxidation reaction produced by it. Due to this, a considerable amount of 3, 3'-dinitroazoxybenzene was always obtained in the final results, while only a small quantity of 1, 3-dinitrobenzene remained at the end of the reaction.*

2,4-Dinitrophenol, another reaction product, was apparently formed by further partial oxidation of the intermediate 2, 4-dinitrophenyldiimine to the corresponding diazo compound which then was decomposed in the usual manner (see [4, 5]).

Investigation of the mechanism of 2, 4-dinitrophenylhydrazine breakdown taking place under the same conditions as the oxidative-hydrolytic cleavage of the 2, 4-dinitroazo dye [I; Ar = $C_6H_3(NO_2)_2$-2, 4], clarified as well the nature of the latter process, which, as mentioned above, gave as final products phthalonic and phthalic acids, 2, 4-dinitrophenol and 5-nitro-1, 2, 3-benztriazole. In this case, after the hydrolysis of the azo dye quinoid form [II; Ar = $C_6H_3(NO_2)_2$-2, 4] to 2-hydroxy-1, 4-naphthaquinone and 2, 4-dinitrophenylhydrazine (scheme 2) two series of interconnected, parallel reactions took place (see [6]). On the one hand there is the previously mentioned hydrolytic cleavage of hydroxynaphthaquinone produced to o-acetylphenylglyoxalic acid, which then acts as a reducing agent and is finally oxidized to phthalonic and phthalic acids. On the other hand, the initially formed arylhydrazine was converted to the 3-oxide of 5-nitro-1, 2, 3-benztriazole which acted as an oxidizing agent and was reduced to the corresponding benztriazole. The main steps in these reactions are whown in diagram 2 and do not require a more detailed explaination.

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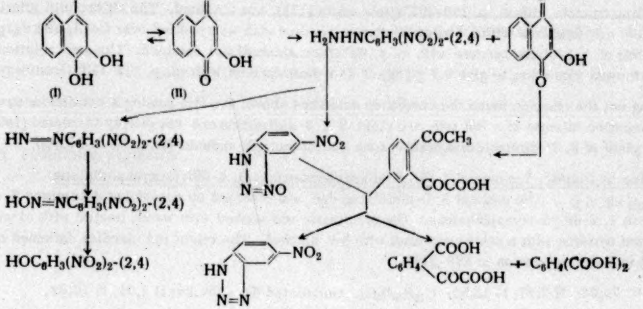
* When the process was carried out not in an inert gas atmosphere, but with atmospheric oxygen present, then, on the contrary, the yield of 1, 3-dinitrobenzene rose sharply while the yield of 3, 3'-dinitroazoxybenzene fell correspondingly. (see Experimental section, Experiment 2).



EXPERIMENTAL

Oxidative-hydrolytic cleavage of 1-(2',4'-dinitrobenzeneazo)-3,4-dihydroxynaphthalene [I; Ar = $C_6H_3(NO_2)_2$-2,4]

The original 2, 4-dinitroazoe dye was obtained by combining diazotized 2, 4-dinitroaniline with 1, 2-dihydroxynaphthalene. The precipitate was washed with water, stirred twice with hot alcohol, recrystallized from chlorobenzene and washed with benzene. Long, dark crimson needles were obtained. Decomp. at 282-283°.

Found %: C 54.20; H 2.87; N 15.58. $C_{16}H_{10}O_6N_4$. Calculated %: C 54.24; H 2.84; N 15.82.

In carrying out the cleavage process we used the apparatus and kept to the conditions and working procedures described in [1] (Experiment 1). 14 g of 2, 4-dinitroazo dye and 3.5 liters of 1% aqueous NaOH were boiled for 7.5 hours in a stream of nitrogen. The solution was acidified with 60% H_2SO_4, the dark precipitate produced was filtered off and the filtrate was extracted 5 times with chloroform and then 5 times with ether. The chloroform and ether solutions were washed with water, boiled with charcoal and dried (the first over $CaCl_2$, the second over Na_2SO_4), after which the solvents were distilled off. From the chloroform solution was obtained 1.13 g of 2, 4-dinitrophenol with m. p. 112-113° (from water); its acetyl derivative had m; p. 72° [7]. From the ether solution was isolated 1.08 g of 5-nitro-1, 2, 3-benztriazole with m. p. 208-209° (from water); the acetyl derivative had m. p. 146° (from toluene [8]). The acidic aqueous solution (remaining after extraction with chloroform and ether) was neutralized to pH 6-6.5 and was boiled down to 200 ml in a stream of nitrogen. The mineral salts which separated were filtered off and the filtrate was strongly acidified with 60% H_2SO_4 and was extracted with chloroform 5 times and with ether 7 times. 0.07 g of 5-nitro-1, 2, 3-benztriazole (m. p. 209°) was isolated from the chloroform solution. From the ether solution was obtained 0.5 g of an oily crystalline residue, which was a mixture of phthalic and phthalonic acids. Crystals of phthalic acid were separated from the oil and phthalonic acid was isolated from the latter in the form of its quinoxaline derivative with m. p. 238-239° (from alcohol; [9], Experiment 2b).

Carrying out the reaction as described above gave a 15.5% yield of 2, 4-dinitrophenol and a 17% yield of 5-nitro-1, 2, 3-benztriazole. If the volume of 1% NaOH solution was increased 4 times then the yield of the first of these materials was increased to 20% and that of the second to 31%.

2. The behavior of 2, 4-dinitrophenylhydrazine on heating with an alkaline solution. The reaction was carried out exactly as described in Experiment 1. 10.54 g of 2, 4-dinitrophenylhydrazine and 4.5 liters of 1% aqueous NaOH were taken. On completion of the reaction, the pH of the solution was brought to 6-6.5 by the addition of 25% H_2SO_4. 4.55 g (58%) of 3, 3'-dinitroazoxybenzene was filtered off and was purified by recrystallization from alcohol in the presence of charcoal. M. p. 142-143°. For characterization, this was converted into 3, 3'-dinitro-4-hydroxyazobenzene with m. p. 172-173° (from chloroform [10]), by heating with H_2SO_4. The aqueous filtrate was strongly acidified with 60% H_2SO_4, filtered and extracted first 5 times with chloroform and then 5 times with ether. The chloroform and ether solutions were washed with water and boiled with charcoal. The ether solution was dried over Na_2SO_4 and the ether was distilled off. 1.32 g (13.7%) of the 3-oxide of 5-nitro-1, 2, 3-benztriazole with m. p. 190-191° (from water [11]), was obtained. The chloroform solution was boiled down to 100 ml, extracted with a 10% soda solution, washed with water, dried over $CaCl_2$ and evaporated down. 0.5 g (5.5%) of 1, 3-dinitrobenzene with m. p. 89° (from alcohol) was obtained. The soda solution was acidified and extracted with ether to give 0.1 g (1%) of 2, 4-dinitrophenol with m. p. 112-113° (from water).

By carrying out the reaction under the conditions described above, but also passing a continuous stream of air through the reaction mixture at a fast rate, the yield of 1, 3-dinitrobenzene was sharply increased (from 5.5 to 22%) and the yield of 3, 3'-dinitrohydroxyazobenzene correspondingly reduced (from 58 to 38.5%).

3. Oxidative-hydrolytic cleavage of 1-(3', 5'-dinitrobenzenazo)-3, 4-dihydroxynaphthalene Ar = $C_6H_3(NO_2)_2$-3, 5]. The original 3, 5-dinitroazo dye was obtained by combining diazotized 3, 5-dinitroaniline with 1, 2-dihydroxynaphthalene. The precipitate was washed with water, heated with alcohol and recrystallized from pyridine with a subsequent wash with hot alcohol. The bright red needles darkened at about 265° and melted with decomposition at 278-279°.

Found %: C 54.00; H 2.97; N 15.50. $C_{16}H_{10}O_6N_4$. Calculated %: C 54.24; H 2.84; N 15.82.

In carrying out the cleavage process we used the apparatus and kept to the conditions and working procedures described in [1] (Experiment 1). Six grams of dye and 4 liters of phosphate buffer solution (pH 9.17, 0.1 molar) were boiled in a stream of nitrogen for 15 hours. The solution was brought to pH 6-6.5 with 25% H_2SO_4 and then the dark brown precipitate (5.2 g) of the products of resinification and condensation of the original azo dye were filtered off. The filtrate was evaporated down to 300 ml, strongly acidified with 60% H_2SO_4, filtered and extracted many times, first with chloroform and then with ether. A small amount of phthalic acid was separated from the ether extract after it had been boiled with charcoal.

SUMMARY

1. Oxidative-hydrolytic cleavage of 1-(3',5'-dinitrobenzeneazo)- and 1-(2,4-dinitrobenzeneazo)-3,4-dihydroxynaphthalene was examined. The first of these similar to 1-benzoneazo-3,4-dihydroxynaphthalene, investigated earlier, was very easily changed, even on boiling with an aqueous solution having a pH of ~9; the second was much more stable and underwent cleavage only on prolonged boiling with 1% alkali solution.

2. It was shown that the end products of cleavage of 2, 4-dinitroazo dyes were phthalonic and phthalic acids, 5-nitro-1, 2, 3-benztriazole and 2, 4-dinitrophenol.

3. In elucidating the formation mechanism of these compounds, the course of cleavage of 2, 4-dinitrophenylhydrazine by aqueous alkali was studied in addition.

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QUATERNARY AMMONIUM COMPOUNDS

II. THE FORMATION OF TETROLIC ACID BY REACTION OF TRIMETHYL-(2, 2, 3, 3,-TETRACHLOROBUTYL)-AMMONIUM IODIDE WITH AQUEOUS ALKALI

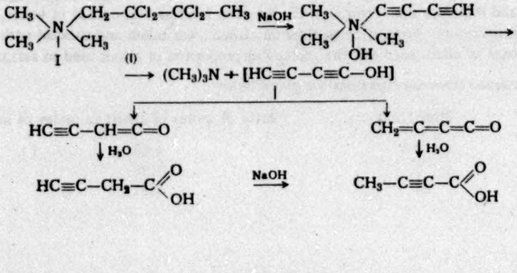
A. T. Babayan and A. A. Grigoryan

In a previous report [1] on the dehydrochlorination of quaternary ammonium salts containing the radical 3-chlorobuten-2-yl, the dependence of the reaction rate on the nature of the nitrogen was clearly shown. While compounds with a quaternary ammonium nitrogen were easily dehydrochlorinated by aqueous alkali, the corresponding tertiary amines were not changed at all under the same conditions. The facility of dehydrochlorination of quaternary ammonium salts, containing halides in the γ-position to the nitrogen, may be explained by the lability of the hydrogen atom in the β-position.

It was interesting to follow the reaction of aqueous alkali on quaternary ammonium salt not containing hydrogen in the β-position to the nitrogen. Trimethyl-(2, 2, 3, 3,-tetrachlorobutyl)-ammonium iodide (I) was selected as this type of compound. The original 1-dimethylamino-2, 2, 3, 3,-tetrachlorobutane was obtained by chlorination of 1-dimethylaminobutane in hydrochloric acid solution with 82-90% yield. The chlorination took place very smoothly and resulted in the addition of four chlorine atoms at the multiple bond. A small amount of 1-dimethylamino-2, 3,-dichlorobutene-2, that is from the addition of two chlorine atoms, was also isolated.

The investigation of the trimethyl-(2, 2, 3, 3-tetrachlorobutyl)-ammonium iodide reaction with aqueous alkali showed that in 2-3 hours at room temperature all four chlorine atoms were converted into the ionic state. The reaction was followed by the increase in concentration of halide ions in the solution, as well as by alkali consumption. The halide ion content after 3 hours corresponded to the theoretical (95.5%); titration results indicated, however, that alkali was used not only for dehydrochlorination. The smell of trimethylamine appeared quite soon. This indicated that under treatment with aqueous alkali at room temperature, trimethyl-(2, 2, 3, 3-tetrachlorobutyl)-ammonium iodide was not only completely dehydrochlorinated but that it also underwent a further cleavage to liberate trimethylamine. The fate of the fourth radical was not clear.

On the basis of the results obtained, the following reaction course seemed possible:



$$(CH_3)_3N + [HC{\equiv}C{-}C{\equiv}C{-}OH]$$

$$HC{\equiv}C{-}CH{=}C{=}O \xrightarrow{H_2O} HC{\equiv}C{-}CH_2{-}COOH \xrightarrow{NaOH} CH_3{-}C{\equiv}C{-}COOH$$

$$CH_2{=}C{=}C{=}C{=}O \xrightarrow{H_2O} CH_3{-}C{\equiv}C{-}COOH$$

Thus, the formation of either ethynylacetic or tetrolic acid would be expected. Actually, by acidifying the reaction mixture and extracting it with ether, an acid was separated with m. p. 78°. The melting point of ethynylacetic acid is 83-83.5° [2], while that of tetrolic is 78° [3]. In view of the closeness of the melting points, tetrolic acid was synthesized for identification [4] and this had m. p. 76° which was not depressed by admixture with the acid we isolated. Furthermore, addition compounds with mercuric chloride [5] were obtained both for tetrolic acid and for the acid produced by us. These compounds were also identical. When recrystallized from methyl alcohol they had m. p. 120° which corresponded to literature data [5] and was not depressed by mixing. The yield of tetrolic acid was 70%.

The possibility exists that tetrolic acid was not the only, or even the initial, reaction product. It is possible that it was formed together with ethynylacetic acid or even as a result of isomerization of the initially formed ethynylacetic acid in the alkaline medium.

EXPERIMENTAL

Preparation of 1-dimethylamino-2, 2, 3, 3-tetrachlorobutane. a) 430 g of chlorine was passed into a solution of 242.5 g of 1-dimethylaminobutene-2 in 350 ml of 34% hydrochloric acid. The reaction product was isolated by making the solution alkaline with potash and extracting with ether. After distilling off the ether the residue crystallized. Pure crystals (364 g) were obtained by separating the crystalline material and washing with small portions of ether. Distillation of the filtrate gave 22 g of liquid, 125 g of crystalline material and 29 g of undistillable residue. 489 g (82%) of crystalline product was obtained by this method. B. p. 114-115° (13 mm), m. p. 46-47°.

Found %: N 6.07. $C_6H_{11}NCl_4$. Calculated %: N 5.85.

The hydrochloride melted at 217°; the picrate at 177° after recrystallization from alcohol.

The liquid product had the following properties: b. p. 71-75° (19 mm) d_4^{20} 1.0999, n_D^{20} 1.4737, MR_D 42.89; calc. 43.14.

Found %: N 8.27. $C_6H_{11}NCl_2$. Calculated %: N 8.33.

M. p. of picrate 156.59°; methiodide 225°.

Found %: I 40.49. $C_7H_{14}NCl_2I$. Calculated %: I 40.90.

b) Chlorine was passed through a solution of 48.5 g of 1-dimethylaminobutene-2 in 100 ml of 34% hydrochloric acid. A total of 75 g of chlorine was absorbed. Then the mixture was neutralized with a concentrated potash solution. The crystalline amine was filtered off and washed many times with water. After drying the crystals had m. p. 46-47°. The yield of 1-dimethylamino-2, 2, 3, 3-tetrachlorobutane was 108 g (90.3%).

Trimethyl-(2, 2, 3, 3-tetrachlorobutyl)-ammonium iodide. A solution of 21.3 g of methyl iodide in 60 ml of acetone was poured into 23.9 g of 1-dimethylamino-2, 2, 3, 3-tetrachlorobutane. The crystals deposited after three hours heating on a boiling water bath were filtered off and washed with alcohol. The yield was almost quantitative. After recrystallization from methyl alcohol the m. p. was 187°.

Found %: I 32.95. $C_7H_{14}NCl_4I$. Calculated %: I 33.30.

Reaction of Trimethyl-(2, 2, 3, 3-tetrachlorobutyl)-ammonium iodide with aqueous alkali. To 1.0068 g of trimethyl-(2, 2, 3, 3-tetrachlorobutyl)-ammonium iodide was added an aqueous solution containing 0.01485 mole of caustic potash. The total weight of solution and salt was 10.8179 g. On mixing the alkali with the salt, heat was evolved and therefore the vessel with the reaction mixture was cooled in water. The solution was left to stand at room temperature. From time to time an aliquot was taken and titrated with 0.1 N sulfuric acid to determine the amount of alkali used and the molecular proportion of alkali used to salt taken, was calculated.

The data obtained from the titrations are given below.

Time (in hours)	Ratio of moles of alkali to moles of salt
1.5	4.65
3	4.95
24	4.87

The data obtained show that already after 3 hours, 4.95 moles of alkali had been used up per mole of salt.

It was also determined that after 24 hours the amount of ionic halide in the solution was 95.5%.

Preparation of tetrolic acid. A solution of 48 g of caustic soda in 40 ml of water was added over 20 minutes to 76.2 g of trimethyl-(2, 2, 3, 3-tetrachlorobutyl)-ammonium iodide in 40 ml of water at −10°. The reaction proceeded with the evolution of heat and was practically complete after 1 hour. The trimethylamine evolved during the reaction was trapped in a bubbler with sulfuric acid. After 1 hour the reaction mixture was washed with ether and then the water layer was carefully acidified with hydrochloric acid and extracted many times with ether. The combined ether extracts were dried over sodium sulfate. After evaporating off the ether the residue (11.8 g, 70.2%) completely crystallized. After recrystallization from benzene, this material melted at 78-78.5°. Admixture with authentic tetrolic acid did not depress the melting point.

Found %: C 57.06; H 4.95. M 88. $C_4H_4O_2$. Calculated %: C 57.14; H 4.76. M 84.

0.2 g of the crystals was dissolved in 2 ml of a saturated solution of mercuric chloride in saturated sodium chloride solution [5]. The crystals which separated out over 20 minutes were filtered off and washed with water. After recrystallization from methyl alcohol they had m. p. 120°. The melting point was not depressed by mixing with the compound of tetrolic acid with mercuric chloride, i. e. α-chloromercuri-β-chlorocrotonic acid, melting at 120°.

SUMMARY

1. Chlorination of 1-dimethylaminobutene-2 in hydrochloric acid solution gave 1-dimethylamino-2, 2, 3, 3-tetrachlorobutane, which is described for the first time.

2. The reaction of 1-dimethylamino-2, 2, 3, 3-tetrachlorobutane methiodide with aqueous alkali led to complete dehydrochlorination and cleavage of the salt with the formation of trimethylamine and tetrolic acid.

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Institute of Chemistry, Academy of Sciences of the Armenian SSR.

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*T. p. = C. B. Translation pagination.

The data obtained show [illegible]

It was also established that after 24 hours the [illegible]

[illegible]. A solution of 36 g of [illegible] trimethyl[illegible]. The reaction proceeded with the evolution of heat and [illegible]. The [illegible] evolved during the reaction was trapped in a bubbler with [illegible]. After 1 h [illegible]. [illegible] crystallized. [illegible] not depress the melting point.

Found %: [illegible]. Calculated %: [illegible].

[illegible]

SUMMARY

1. [illegible]

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LITERATURE CITED

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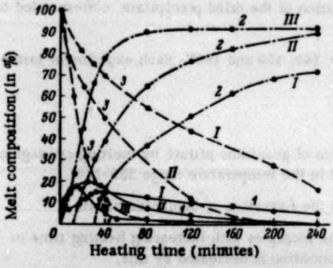
MECHANISM OF GUANIDINE NITRATE FORMATION BY AMMONIOLYSIS OF CYANOGUANIDINE

S. N. Kazarnovsky and N. I. Moshchanskaya

Guanidine salts are finding an ever widening industrial application, at the present time, especially in organic synthesis. The general method used for producing guanidine salts is by fusing cyanoguanidine with ammonium salts [1]. A reaction mechanism for the formation of guanidine salts through biguanidine was suggested and proved experimentally by Blair and Braham [2] and, simultaneously, by Davis [3]. Melamine and a product described by the authors as a mixture of ammeline and ammelide were side products of the synthesis of guanidine salts [3, 5].

The aim of the present work was to investigate in detail the reaction kinetics of guanidine nitrate formation over the temperature range 130-160°.



Changes in content of biguanide nitrate, guanidine nitrate and cyanoguanidine in a cyanoguanidine ammonium nitrate melt, in relation to heating time at 130° (I), 140° (II), 150° (III).
1) Biguanide nitrate; 2) guanidine nitrate;
3) cyanoguanidine.

The investigation results are given graphically in the diagram; the heating time in minutes is plotted on the abscissa and the melt content of biguanide and guanidine nitrates (in % of the theoretical) and cyanoguanidine (in percentage of initial cyanoguanidine) are on the ordinate. *

As can be seen from the graph at all temperatures investigated the formation of biguanide nitrate started immediately from the moment the reaction mixture was placed in the thermostat. Its content in the melt increased at first, reaching a maximum, and then decreased. Further decrease in biguanide nitrate content occurs at an increasing rate with an increase in temperature. The formation of guanidine in the melt began earlier, on increasing the temperature. Its content in the melt, in contrast to biguanide nitrate, increased constantly. With an increase in temperature the guanidine nitrate content increased at a faster rate. The biguanide nitrate content started to fall off when its formation rate became less than that of guanidine nitrate. The unreacted cyanoguanidine content of the melt decreased more rapidly with increasing temperature.

It appeared that the melts contained only an insignificant amount of melamine (1-2 %). Materials insoluble in water (ammeline and ammelide) were practically non-existent in the samples, and were not present as more than a tenth of a percent.

The balance (total on cyanoguanidine) for the separate analyses of the melts was 90-104%.

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*The curves obtained for 160° are similar in character to those for 150°.

EXPERIMENTAL

A mixture of cyanoguanidine and ammonimn nitrate, in the molecular proportions of 1 : 2.4, was placed in glass tubes (6.2 g of mixture in each), which were placed in a thermostat, where they were maintained at a given temperature with an accuracy of ± 1.5°, and were removed from it after a definite time interval. The weight of the tubes before and after heating was constant. To obtain a uniform liquid melt, before placing in the thermostat, the tubes with the reaction mixture were heated for 30 min at 120° in a glycerine bath. Analysis showed that 3.2% of biguanide nitrate was formed in the mixture by this and that 29.2% of unreacted cyanoguanidine remained, which was allowed for in constructing the graphs.

In the samples obtained, the biguanide and guanidine nitrate contents were determined. In some tubes the content of unreacted cyanoguanidine was determined. Besides this, in some samples the content of melamine and substances insoluble in water (ammeline and ammelide) was determined. The biguanide mitrate content was determined by Garby's method [4] with the following changes introduced by us: in preparing the precipitating reagent a 7% solution of mannitol was used and instead of 40 ml of concentrated ammonia, 90 ml; as an indicator we used indigo carmine. The guanidine nitrate content was determined by the generally accepted Fotsarik method [5]. The guanidine nitrate content was determined using 5 ml of a solution obtained from 4 g of melt in 100 ml of water and the biguanide nitrate content was determined on 25 ml of this solution.

The unreacted cyanoguanidine content of the melts was determined by Byukenen's method [6, 7]. For the analysis we took 25 ml of a solution prepared from 1 g of melt in 100 ml of water. For the analysis of melts with a high guanidine nitrate content (greater than 50% of the weight of melt), 0.5 g of melt was dissolved in 50 ml of water and the cyanoguanidine content determination was carried out on the whole solution.

The melamine content of the melts was determined by its precipitation as the cyanurate by the method developed in the laboratory for the technology of organic materials of the Gorki Polytechnic Institute, in which 0.5 g of the melt was dissolved in 50 ml of water, the insoluble residue was filtered off and 100 ml of 0.15% cyanuric acid solution was added to the filtrate. The composition of the dried precipitate corresponded to the formula $C_3H_6N_6 \cdot C_3H_3O_3N_3$ [8].

The investigation of the kinetics was carried out at 130, 140, 150 and 160°. Each experiment lasted for 4 hours.

SUMMARY

1. We investigated the reaction kinetics of the formation of guanidine nitrate by melting cyanoguanidine with ammonium nitrate in the molecular proportions of 1 : 2.4 in the temperature range 130-160°.

2. The formation of guanidine nitrate proceeds through the formation of biguanide nitrate.

3. The guanidine nitrate content of the reaction mixture increases with increasing heating time at constant temperature; the reaction rate of guanidine nitrate formation is decreased by this.

4. The rate of guanidine nitrate formation increases with raising of the temperature.

5. Only melamine, of the side products of the reaction (triazine derivatives), was formed under the conditions of our experiment (with small quantities of reaction mixture).

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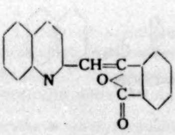
Gorki Polytechnical Institute.

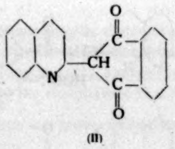
INVESTIGATION IN THE FIELD OF TAUTOMERIC COMPOUNDS

XXII. THE LABILITY OF HYDROGEN ATOMS OF THE QUINALDINE METHYL GROUP

A. E. Porai-Koshits* and I. I. Chizhevskaya

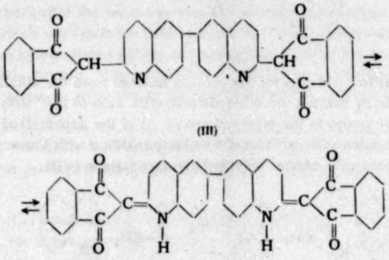
The capacity of compounds with labile methyl hydrogen atoms to condense with carboxylic anhydrides was first illustrated by the reaction of quinaldine with phthalic anhydride [1]. On studying the mechanism of this reaction, it was established [2] that the condensation of quinaldine with phthalic anhydride at temperatures up to 150° resulted in isoquinophthalone formation (I), which is a phthalyl derivative –3-(quinaldilen)-phthalide; isomeric quinophthalone (II), which is an indandione-1, 3 derivative, was formed by raising the condensation temperature from 150 to 240°.


(I)


(II)

Quinophthalone, after sulfonation, has been used as a valuable acid dye, known as "quinoline yellow".

A. E. Porai-Koshits and A. I. Kulikov [3], on the basis of the analogous structure of acid and substantive azo dyes, condensed biquinaldine with phthalic anhydride to synthesize a biquinophthalone derivative, which was the reaction product of 2 moles of phthalic anhhdride with 1 mole of biquinaldine. A substantive dye – biquinoline yellow, α, α'-bis-(indandion-1, 3-yl-2)-biquinoline (III), which dyed cotton yellow in a soda-lye bath was obtained by sulfonation of the condensation product.


(III)

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*Deceased.

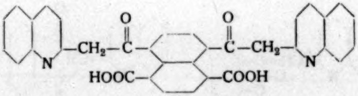
The dye synthesized was the first sample of the new type of substantive dye with no azo group in the molecule. The new substantive dye was an improvement on benzidine azo dyes in its stability to acid.

As further research into ways of synthesizing the new type of substantive dyes, for the theoretical interest as well as the technical application, we investigated the condensation reaction of quinaldine with the dianhydrides of naphthalene-and perylenetetracarboxylic acids. Materials containing a long chain of conjugated double bonds would be expected from the above condensation. The sulfonation of these materials should result in the production of the new type of substantive dyes, while the presence of carbonyl groups in the conjugated chain gave the possibility of use as vat dyes.

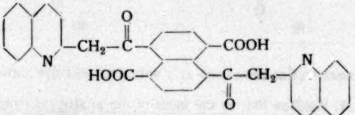
There is no data in the literature on the condensation reaction of materials having labile methyl hydrogen atoms, with tetracarboxylic dianhydrides and this reaction was investigated for the first time by us, using quandine as the example. Condensation of quinaldine with naphthalenetetracarboxylic dianhydride was carried out by heating 2 moles of quinaldine with 1mole of naphthalenetetracarboxylic dianhydride. Two products were obtained from the condensation, one of which was soluble in aqueous alkali and the other insoluble.

By acidifying the alkaline solution a reddish-brown material was isolated which reacted with hydroxylamine and phenylhydrazine,and on treatment with caustic potash and silver nitrate, formed potassium and silver salts.

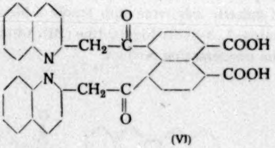
Elementary analysis of the material isolated from the alkali solution, as well as analysis of derivatives produced, showed that the material investigated was possibly a naphthalene diketodicarboxylic acid corresponding to one of the following structural formulas: 5, 8-di-(quinaldilen-oxymethyl)- naphthalene-1, 4-dicarboxylic acid (IV), 4, 8-di-(quinaldilen-oxymethyl)- naphthalene-1, 5-dicarboxylic acid (V) and 1, 8-di-(quinaldilen-oxymethyl)-naphthalene-4, 5-dicarboxylic acid (VI).



(IV)

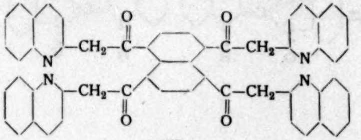


(V)



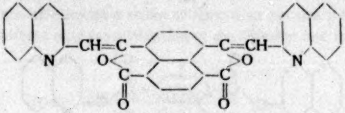
(VI)

A strong argument against formula (VI) for the product isolated from the alkali solution, was the impossibility of obtaining the anhydride by heating the diketodicarboxylic acid to 250° with the separation of 1 water molecule from the two carboxyl groups in the peri-position (4, 5) of the naphthalene nucleus, as well as the impossibility of obtaining the condensation product of 4 moles quinaldine with 1 mole of naphthalenetetracarboxylic anhydride, namely, 1, 4 ,5, 8-tetra-(quinaldilen-oxymethyl)-naphthalene (VII).

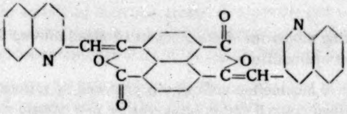


(VII)

A product, differing from the diketodicarboxylic acid by two water molecules was produced when the latter was heated at 230-250°. The product obtained was, apparently, a diketo-dicarboxylic lactone – the dilactone of a di-(quinaldilen-oxymethyl)-dicarboxylic acid of naphthalene, which corresponded to 5, 8-di-(quinaldilen-oxymethyl)-naphthalene-1, 4-dicarboxylic dilactone (VIII) or 4, 8-di-(quinaldilen-oxymethyl)-naphthalene-1, 5-dicarboxylic dilactone (IX).



(VIII)



(IX)

The condensation of 1 mole of naphthalene-tetracarboxylic dianhydride with 4 moles of quinaldine gave products identical with those obtained by condensing only 2 moles of quinaldine with 1 mole of naphthalene-tetracarboxylic dianhydride. The product, corresponding to formula (VII), apparently, was not formed due to steric hindrance (entry of a second quinaldine molecule into the naphthalene in a position peri to the first).

Thus the problem of the diketocarboxylic acid structure was reduced to establishing its steric structure.

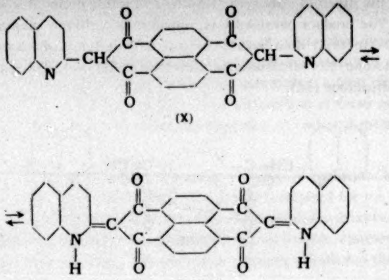
The method generally used for separating cis and trans isomers of naphthalene- and perylenetetracarboxylic acid diimidazole derivatives, based on the different solubilities of these isomers in alcoholic caustic potash, did not give positive results when applied. No two materials with different solubilities in alcoholic caustic potash were detected.

An attempt to decarboxylate the diketodicarboxylic acid to give 1, 4-or 1, 5-di-(quinolyl-acetophenone)-naphthalene with subsequent oxidation of the latter to a 1, 4- or 1, 5-dicarboxylic acid of naphthalene was unsuccessful. In the decarboxylation experiments we obtained quinaldine and naphthalene; apparently, the cleavage of quinaldine took place first and then the naphthalenetetracarboxylic acids which formed were decarboxylated to give naphthalene.

Investigation of the properties of the second product, produced by quinaldine condensation with naphthalenetetracarboxylic dianhydride which was insoluble in alkali, showed that it was suitable for "vatting", that is, it was soluble in alkaline sodium hydrosulfite solution and was separated from the latter by oxidation of the hydrosulfite solution with atmospheric oxygen. The insolubility of the product obtained in alkali indicated the absence of lactone rings in the latter, while its solubility in alkaline hydrosulfite solution – the presence of carbonyl groups.

Elementary analysis of the alkali-insoluble product showed that its composition was identical with that of the alkali-soluble condensation product of quinaldine with naphthalenetetracarboxylic dianhydride which we had investigated earlier.

By analogy with the similar condensation of quinaldine with phthalic anhydride, which also produces two reaction products (I) and (II), the structural formula 4, 9-di-(α-quinolyl)-4, 9-dihydro-3, 5, 8, 10-tetraoxopyrene (X) seemed possible for the alkali-insoluble condensation product of quinaldine with naphthalenetetracarboxylic dianhydride.



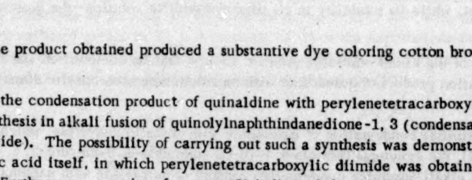
(X)

An examination of the coloring properties of the products obtained showed that it was a vat dye, coloring cotton golden yellow in an alkaline hydrosulfite vat.

A substantive dye, an analog of biquinoline yellow, was produced by sulfonation of the alkali-insoluble product. The substantive dye obtained colored cotton olive-yellow in a caustic soda bath. The color samples were stable to light and acid.

Only one product, insoluble in alkali, was produced by quinaldine condensation with perylenetetracarboxylic dianhydride. Unreacted perylenetetracarboxylic acid was separated by acidifying the alkaline solution. The alkali-insoluble product dissolved well in alkaline sodium hydrosulfite solution and possessed all the properties of a vat dye, coloring cotton red.

Insolubility in aqueous alkali solutions and capacity for vatting as well as elementary analysis data suggested a structure for the condensation product of quinaldine with perylenetetracarboxylic dianhydride corresponding to 2', 2" -di-(α-quinolyl)-2', 2" -dihydro-1', 3', 1", 3" - tetraoxo-3, 4, 9, 10-dibenzperylene (XI), analogous to a similar condensation product of quinaldine with naphthalenetetracarboxylic anhydride.



(XI)

Sulfonation of the product obtained produced a substantive dye coloring cotton brownish-red in a soda-lye bath.

The structure of the condensation product of quinaldine with perylenetetracarboxylic acid (XI) was confirmed by us by its synthesis in alkali fusion of quinolylnaphthindanedione-1, 3 (condensation product of quinaldine with naphthalic anhydride). The possibility of carrying out such a synthesis was demonstrated by the synthesis of perylenetetracarboxylic acid itself, in which perylenetetracarboxylic diimide was obtained by alkali fusion of naphthalic imide [4]. Furthermore, a series of patents [5] indicated the possibility of obtaining several perylenetetracarboxylic acid derivatives from the corresponding naphthalic acid derivatives.

Alkali fusion of quinolylnaphthindanedione-1, 3 gave a product, insoluble in alkali but soluble in an alkaline sodium hydrosulfite solution. The vat color on cotton, and data from spectrophotometric measurements were identical with those of the condensation product of quinaldine with perylenetetracarboxylic dianhydride (XI). The yield of vattable material was doubled. Furthermore, application of the alkali fusion method simplified the synthesis of the vattable material – condensation product of 2 moles of quinaldine with 1 mole of perylenetetracarboxylic dianhydride – and eliminated a series of operations necessary to the synthesis of perylenetetracarboxylic acid dianhydride (sulfuric acid saponification of the diimide and the purification of it and of perylenetetracarboxylic dianhydride).

EXPERIMENTAL

I. Condensation of Quinaldine with Naphthalenetetracarboxylic Anhydride

2.7 g of naphthalenetetracarboxylic dianhydride was ground in a mortar with 3 g of quinaldine and the mixture was transferred to a round bottomed flask, equipped with an air condenser, and was heated 2-2.5 hours at 200-210°. After cooling, the solidified melt was ground to a powder and was treated with boiling 1% hydrochloric acid, after which it was washed with a warm 2% solution of soda and then with water and, finally, it was dried at 100°. It was a reddish-brown powder. M. p. was > 360° and the yield was 3.6 g (70%).

The action of an aqueous caustic soda solution on the condensation product. 10 g of condensation product was boiled with 200 ml of 15% caustic soda solution for 1-2 hours. As the precipitate dissolved, the alkaline solution became intense yellow. The part of the precipitate which did not dissolve in alkali (about 30%), was filtered off, carefully washed with water and dried (product insoluble in alkali). By acidifying the alkaline mother liquor with 10% hydrochloric acid, a brick-red, gelatinous precipitate was separated and the yellow solution was decolorized. The precipitate was filtered off, washed with water and dried at 100° (product soluble in alkali).

Examination of the condensation product which was soluble in alkali. The product was purified by reprecipitating three times with acid from a soda solution, was washed with water until there was no ionic chlorine in the filtrate and was dried in a thermostat at 100-110°. A reddish-brown amorphous powder of 5, 8- or 4, 8-di(quinaldilen-oxymethyl)-naphthalene-1, 4-dicarboxylic acid (IV or V) was obtained. M. p. was greater than 360° and it was soluble in dilute aqueous solutions of ammonia and soda.

Found %: C 73.31, 73.23; H 4.10, 4.07; N 5.50, 5.28. $C_{34}H_{22}O_6N_2$. Calculated %: C 73.64; H 4.00; N 5.05.

The silver salt was prepared from 5 g of the product through the ammonium salt. The yellow, flocculent precipitate of the silver salt was filtered off, washed with alcohol and dried at 70-90°.

Found %: Ag 27.79. $C_{34}H_{20}O_6N_2AG_2$. Calculated %: Ag 28.10.

The potassium salt was prepared by dissolving 5 g of the product in 20 ml of caustic potash solution and evaporating on a water bath until the beginning of crystallization. The precipitate which separated on cooling was filtered off and recrystallized from alcohol. A yellow, finely crystalline powder was obtained.

Found %: K 12.04, 12.15. $C_{34}H_{20}O_6N_2K_2$. Calculated %: K 12.40

The oxime was prepared by boiling 3 g of the potassium salt with the calculated quantity of hydroxylamine hydrochloride in alcohol solution in the presence of soda. After cooling a yellow flocculent precipitate separated. The m. p. was above 360° (from alcohol).

Found %: N 9.30, 9.14. $C_{34}H_{24}O_6N_4$. Calculated %: N 8.95.

The phenylhydrazone was prepared from 3 g of the potassium salt, dissolved in 10 ml of water, by combining with the calculated quantity of phenylhydrazine, dissolved in 50% acetic acid and then diluting with three volumes of water while heating on a water bath. The precipitate which separated on cooling melted above 310° (from a mixture of alcohol and ether).

Found %: N 11.01, 11.60. $C_{46}H_{34}O_4N_6$. Calculated %: N 11.44.

On heating the condensation product at 230-250° for 6 hours, a meterial was obtained which was insoluble in soda and aqueous ammonia, did not react with hydroxylamine and corresponded to 5, 8-di-(quinaldilen-oxymethyl)-naphthalene-1, 4-dicarboxylic dilactone (VIII) or the isomeric 4, 8-di-(quinaldilen-oxymethyl)-1, 5-dicarboxylic dilactone (IX).

Found %: C 78.28, 78.41; H 3.70, 3.17. $C_{34}H_{18}O_4N_2$. Calculated %: C 78.76; H 3.50.

Decarboxylation of the diketo-diacid was carried out by heating with soda lime (1 : 8) at a temperature above 360°; this decomposed the acid into naphthalene, quinaldine and carbon dioxide. About 20% of the starting material was left unchanged.

By heating naphthalenetetracarboxylic dianhydride (2.7 g) with excess quinaldine (8 g), previously ground to a uniform mass in a mortar, at 200-210° for 2-2.5 hours, a material was obtained which was identical with the material obtained by the condensation in Experiment 1.

Examination of the condensation product which was insoluble in alkali. Five grams of the material was heated to 75-80° with 400 ml of alkaline sodium hydrosulfite solution. The precipitate dissolved and the solution was a reddish-brown color. A precipitate was separated by air oxidation and the solution was decolorized.

Cotton was colored green by the hydrosulfite solution but became golden yellow in air. The color was stable to natural light and washing.

The product, which was insoluble in alkali, was purified by "vatting" four times, after which it was carefully washed with hot water and boiling alcohol and dried at 130-140°. The yield of vattable material was 3.75 g. The brick-red powder was insoluble in organic solvents. 4, 9-Di-(α-quinolyl)-4, 9-dihydro-3, 5, 8, 10-tetraoxo-pyrene (X) melted above 360°.

Found %: C 78.12, 78.20; H 3.62, 3.77; N 5.16, 5.03. $C_{34}H_{18}O_4N_2$. Calculated %: C 78.76; H 3.50; N 5.40.

Sulfonation of the alkali-insoluble product. Two grams of the vattable product was heated from 140 to 185° for 6 hours with 12 g of oleum, containing 27% of free SO_3. When a test sample of the sulfonation mixture was soluble in water, the latter was cooled to 80°, then poured into ice-water (50 ml) and salted out with 30 ml of a saturated salt solution. The sodium salt of the sulfonic acid was filtered off, then again dissolved in 100 ml of water and salted out with sodium chloride for the second time. The yield of the sodium salt of the sulfonic acid was 1.4 g. A solution of the sodium sulfonate colored cotton olive-yellow in a soda-lye bath containing Glauber's salt.

II. Condensation of Quinaldine with Perylenetetracarboxylic Dianhydride.

3.9 g of perylenetetracarboxylic dianhydride, prepared by the method developed by A. E. Porai-Koshits in conjunction with I.S. Pavlushenko [4], and 3 g of quinaldine was ground up in a mortar, transfered to a round-bottomed flask, fitted with an air condenser, and heated at 180-200° for 4 hours. After cooling, the solidified melt was ground to a fine powder in a mortar and was treated with 3% caustic potash solution until the solution was no longer yellow. A brick-red precipitate of the unreacted perylenetetracarboxylic dianhydride was separated out on acidifying the alkaline mother liquors. The residue which did not dissolve in 3% caustic potash solution, was filtered off, washed with hot water and alcohol and dried. The powder was a dark red color. The yield was 2.1 g (33%).

Six grams of the condensation product which was insoluble in 3% caustic potash, was heated with 500 ml of a 1% alkaline solution of sodium hydrosulfite to 60-70°; the precipitate dissolved, giving a red-violet solution with a crimson fluorescence. The solution was filtered and oxidized with air, which produced a red-brown precipitate and decolorized the solution. The vatting process was repeated 3 times, after which the precipitate was filtered off, washed with hot water and alcohol and dried. Yield of vat material was 4.78 g (26.7%).

The hydrosulfite solution dyed cotton a dark-violet color which turned red in air. The color was stable to light and to washing.

Analysis of the vatted material – 2', 2"-di-(α-quinolyl)-2', 2"-dihydro-1', 3', 1", 3"-tetraoxy-3, 4, 9, 10-dibenzperylene (XI).

Found %: N 4.68, 4.54. $C_{44}H_{22}O_4N_2$. Calculated %: N 4.36.

Sulfonation of the alkali-insoluble product. Two grams of the vatted material and 16 g of 27% oleum was heated at 180° for 6 hours with mechanical stirring.

At the end of the sulfonation, a test sample showed that the sulfonation mass was only partly soluble in water. After cooling, the sulfonation mass was poured into ice-water, the solution was filtered from the unreacted solid residue and after this the sulfonic acid was salted out of the solution by the addition of saturated salt solution. The yield of sodium sulfonate was 0.75 g.

A solution of the sodium sulfonate dyed cotton a brownish-red color in a soda-lye bath containing Glauber's salt.

III. Condensation of Quinaldine with Naphthalic Anhydride

Two grams of naphthalic anhydride and 1.5 g of quinaldine was ground in a mortar, then heated at 210-220° for 2 hours in a flask with an air condenser. The solidified melt was ground in a mortar, treated with boiling 1% hydrochloric acid and then with a 2% soda solution, washed with water and dried. Light yellow, silky, thread-like crystals were obtained (from glacial acetic acid). The yield of quinolyl-peri-naphthindanedione-1,3; 3.1 g (96%).

A mixture of alkali-soluble and insoluble precipitates was obtained with a lower reaction temperature (180°).

Alkali fusion of the condensation product of quinaldine and naphthalic anhydride. 8.8 g of caustic potash and 1 ml of water were put into a crucible and heated until the alkali fused, after which 2 g of the condensation product of quinaldine and naphthalic anhydride were added and the temperature in the crucible was raised to 295°. After keeping it at this temperature for 15 minutes, the melt was poured into water (60 ml) and was oxidized by passing air for 2 hours. The precipitate which came out was filtered off, washed with water and purified by vatting. The color of the hydrosulfite vat and the coloring of cotton were identical with those for the condensation product of quinaldine and perylenetetracarboxylic dianhydride. The yield of vatted material was 1.3 g (almost 65%).

SUMMARY

1. Quinaldine condenses with naphthalene-and perylene-tetracarboxylic dianhydrides due to the active hydrogen atoms of the methyl group.

2. The condensation products of quinaldine with naphthalene- and perylenetetracarboxylic dianhydrides are vat dyes for cotton and, after sulfonation, are converted into substantive dyes of a new type – analogs of biquinoline yellow.

3. The structure of the vat dye, derived from perylene-tetracarboxylic dianhydride, was established by synthesis of the latter, starting from quinolyl-peri-naphthindanedione-1, 3 (alkali fusion).

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Lensoviet Leningrad Technologic Institute.

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SYNTHESIS OF PROPIONIC ACID-1-C^{14} VIA AN ORGANOLITHIUM COMPOUND

N.F. Novotorov and I.A. Korshunov

The utilization of labeled atoms in investigations presupposes their previous introduction into the molecules of the compounds under investigation. The relatively high cost of certain isotopes and their biological harmfulness necessitates synthesis under conditions rather different from those in the preparation of the normal organic compounds.

Both the Russian and foreign literature contain much data in the form of papers [1-5] and monographs [6] relating to the synthesis of organic acids labeled with radiocarbon. The comparative simplicity of introduction of a labeled carbon group into a molecule, with formation of acid, and the subsequent syntheses on the basis of this product, enable the preparation of diverse organic compounds labeled with radiocarbon. Development of a convenient method of synthesis of labeled carboxylic acids is of particular interest.

The best-known method of preparation of organic acids labeled with the carbon isotope C^{14}, via organomagnesium compounds according to the reaction

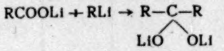
$$RMgI + C^{14}O_2 \rightarrow RC^{14}OOMgI \rightarrow RC^{14}OOH$$

has been applied to the synthesis of a number of labeled acids and has been fully described in the literature [4].

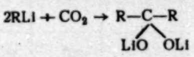
In spite of the great value of the method based on the above reaction, it is not free from defects. The long period of time for the synthesis and later isolation of the end product, as well as its dilution with a carrier, are obstacles to the application of this method to syntheses with weakly enriched preparations (carbon isotope C^{13}). This method is also hardly suitable for preparation of molecules labeled with the short-lived C^{11} isotope.

All these disadvantages are eliminated to a considerable extent by carrying out the synthesis via organolithium compounds. A method of carboxylation of organolithium compounds of the aromatic series is reported in the literature [7]. It involves the action of solid carbon dioxide on organolithium compounds. Depending upon the conditions, the following reactions take place:

$$RLi + CO_2 \rightarrow RCOOLi \qquad (1)$$



$$RCOOLi + RLi \rightarrow R{-}C(OLi)(OLi){-}R \qquad (2)$$



$$2RLi + CO_2 \rightarrow R{-}C(OLi)(OLi){-}R \qquad (3)$$

$$RCOOLi + RLi + CO_2 \rightarrow R{-}CO{-}R + LiCO_3 \qquad (4)$$

$$2RLi + CO_2 \rightarrow R{-}CO{-}R + LiCO_3 \qquad (5)$$

The product of reactions (2) and (3) is transformed after hydrolysis into a ketone [8]. Reactions (4) and (5) can be successfully applied to the synthesis of labeled ketones via organolithium compounds.

The lithium salt of the carboxylic acid, directly obtained in the process of carboxylation, considerably shortens the time for the subsequent operation of isolation of the labeled product and does not require the introduction of a carrier. The duration of the reaction is greatly shortened because the process of carboxylation goes more intensively. By appropriate choice of the reaction temperature, it is possible to obtain salt of acid, ketone or alcohol in dependence upon the experimental conditions.

In connection with this method we must mention that the possibility of using organolithium compounds for preparation of carboxylic acids was first demonstrated by P. P. Shorygin [9]. The latter carboxylated ethyllithium which he had prepared from diethylmercury and metallic lithium.

EXPERIMENTAL

The reaction was conducted in a three-necked pyrex flask of 500 ml volume; the flask was fitted with an induction stirrer, a condenser and a tube with tap for introduction of gases.

Synthesis of ethyllithium. The method was that proposed for preparation of crystalline organolithium compounds [10]. 7 g metallic lithium was placed in the reaction flask from which the air had been driven out with dry nitrogen. The lithium was charged in with a small quantity of pentene (20-30 ml) obtained by dehydration of isoamyl alcohol over china clay catalyst (the fraction with b.p. 28-36° was taken). Ethyl bromide (55 g) was mixed with 180-200 ml pentene and this mixture was added dropwise from a funnel to the reaction vessel in the course of 6 hours. The reaction went with slight development of heat at 20-22°. Its completion could be judged by the completeness of passage of the metallic lithium into the greyish-violet precipitate of ethyllithium which is insoluble in pentene.

The precipitate of ethyllithium was dissolved in 200 ml n-hexane and the solution filtered. The pentene had previously been distilled off. The yield was determined by titration of the lithium hydroxide with 0.1 N HCl. The hydroxide was obtained by decomposition with water of definite volume of the solution of ethyllithium in n-hexane obtained after filtration. Yield of ethyllithium 78%.

Preparation of propionic acid-1-C^{14}. Labeled carbon dioxide was bubbled into a reaction vessel containing 6 g ethyllithium in 250 ml n-hexane at a pressure of 200-300 mm. A system of bubblers enabled unreacted $C^{14}O_2$ to be recirculated to the reaction mixture. Carboxylation was effected at low temperatures (of the order of -30 to -70°). This method of carboxylation was very much more effective both for organolithium and organomagnesium compounds. The rate of carboxylation under these conditions reached 400-500 ml CO_2/min. (see Table 1). The progress of carboxylation was easily followed from the formation of the n-hexane-insoluble lithium salt of propionic acid. The salt was separated from the n-hexane on a glass filter (No. 3). The white precipitate consisted entirely of lithium propionate with a trace of lithium hydroxide; the latter was determined by titration of a weighed sample of the salt with unlabeled propionic acid. 1.18 g salt contained 0.006 g lithium hydroxide. Yield of lithium propionate 97-98%.

Carboxylation of Ethyllithium with Labeled Carbon Dioxide

Amount in solution		$C^{14}O_2$ consumed in carboxylation			Rate of carboxylation (ml/min)	Carboxylation temperature	Propionic acid obtained			Yield of acid (in %)	
ethyllithium (g)	n-hexane (ml)	g	specific activity, $\frac{imp/min}{mmol}10^5$	total activity, $\frac{impulses}{min}10^7$			g	$C^{14}O_2$ equivalent		on weight	on total activity of $C^{14}O_2$
								specific activity, $\frac{imp/min}{mmol}10^5$	total activity, $\frac{impulses}{min}10^7$		
3.3	150	4	12	10.9	380	-30°	0.4	12.0	0.87	6	8 ± 3
3	100	3.65	12	10.0	400	-40	1.6	12.0	2.9	26	29 ± 3
6	250	7.3	12	20.0	350	-60	10.5	12.0	17.6	86	89 ± 3
8.5	350	10.3	9.2	21.6	500	-70	16.4	9.21	21.0	95	97 ± 3

Pure propionic acid was prepared by dissolving the precipitate of lithium propionate on a glass filter with the equivalent amount of 6 N sulfuric acid at room temperature. The carboxyl-labeled propionic acid was extracted with ethyl ether and the extract dried with sodium sulfate; the ether was driven off and the residual acid fractionated in a column. Yield 95%. B.p. 141°; n_D^{20} 1.3875. Radiochemical yield 96 ± 3%.

Radiochemical Examination of the Product

Propionic acid-1-C^{14} was introduced into a Geiger counter in the form of vapor and its activity determined directly. The components of the mixture in the counter had the following partial pressures: CO_2, 48 mm; ethyl alcohol, 12 mm; propionic acid-1-C^{14}, 2-4 mm: the working voltage of the counter was 2000 V. The measurement error was 10%.

A more accurate method of determination of the activity of the product consists in microcombustion of the propionic acid-1-C^{14} or its salt [11] to $C^{14}O_2$, followed by measurement of the activity of the carbon dioxide in the Geiger counter. The components of the mixture had the following partial pressures in the counter: $C^{14}O_2$, 48 mm; C_2H_5OH, 12 mm; the working voltage of the counter was 2000 V. The error of measurement was 0.5-1%.

The conditions of each experiment and the yields (by weight and radiochemically) are detailed in the table.

SUMMARY

1. Carboxylation of ethyllithium at -70° leads to formation of the lithium salt of propionic acid in a yield of 97-98%.

2. The reaction temperature during carboxylation markedly influences the yield of the salt of the acid.

3. Details are given of the radiochemical analysis of propionic acid-1-C^{14}; the specific activity of the propionic acid, calculated per atom of C^{14}, agrees with the specific activity of the original $C^{14}O_2$.

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Radiochemical [illegible]

Propionic acid-1-C^{14} was injected into a Geiger counter [illegible] determined directly. The composition of the [illegible] in the counter and the [illegible] CO_2, [illegible] ethyl alcohol, 15 [illegible] propionic acid-1-C^{14}, [illegible] The measurement error was [illegible].

A more accurate method of [illegible] the propionic acid-1-C^{14} or [illegible] in the Geiger counter. The [illegible] $C^{14}O_2$ [illegible] The error was [illegible].

The results of [illegible]

SUMMARY

1. The [illegible] propionic acid [illegible]

2. The [illegible]

3. Details are given of the [illegible] propionic acid-1-C^{14} [illegible]

LITERATURE CITED

(1) [illegible]

(2) [illegible]

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(6) M. Calvin, Ch. Heidelberger, [illegible]

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COMPOUNDS LABELED WITH C^{14} AND N^{15}

IV. SYNTHESIS OF "KEY" COMPOUNDS*

V.I. Maimind, B.V. Tokarev, E. Gomes, R.G. Vdovina,
K.M. Ermolaev and M.M. Shemyakin

Notwithstanding certain statements to the contrary [2], the preparation of labeled compounds is often associated with specific difficulties. In many cases, for example, it is necessary to develop new methods or to modify existing methods of synthesis, due to the exceptional value and high cost easily accessible compounds like ammonia and barium carbonate which are normally very cheap. Additional difficulties arise when it is necessary to work with very small amounts of substances and to recover the labeled compound which has not entered into reaction or which has participated in secondary reactions. It may also be desired to recover the labeled substance in the undiluted state and in a form convenient for later utilization.

Special attention must be given to the preparation of key substances of potential value as starting materials for synthesis of a wide range of labeled compounds. For instance, with labeled potassium phthalimide a large number of diverse N^{15}-containing compounds may be synthesized; labeled nitric and nitrous acids and their salts are equally useful. On the other hand for the synthesis of many types of C^{14}-containing compounds it suffices to have available only one key substance – labeled hydrocyanic acid.

In the course of a series of investigations on labeled compounds, we have recently developed methods of micro and semimicro synthesis of the above-mentioned key substances which are distinguished by simplicity of procedure and apparatus, by a small number of steps, by high yield, and by the purity of the products obtained.

The methods of synthesis of labeled phthalimide, potassium phthalimide, nitric acid, nitrates and nitrites were carried out starting from 10-150 mmol $N^{15}H_3$; the method for hydrocyanic acid can start from 0.5-15 mmol $BaC^{14}O_3$.

We prepared phthalimide-N^{15} in nearly quantitative yield and in the substantially pure form by dehydration of ammonium acid phthalate; the method differs from that previously described [3] in respect to the procedures for isolation and purification of phthalimide. Potassium phthalimide-N^{15} can be conveniently prepared by the action of an alcoholic solution of potassium ethoxide (in place of the usually recommended aqueous alcoholic solution of KOH) on a solution of phthalimide in anhydrous alcohol. By this modification the yield of potassium phthalimide was raised from 85-90% [4] to 98-99%, and the product was absolutely pure.

The important key substance nitric acid-N^{15} was formerly prepared by Clusius et al [5,6] by oxidation of N_2O (or N_2) in the voltaic arc followed by the action of oxygen and water or (KOH) on the N_2O_4. This method is unattractive, however, if the starting compound is $N^{15}H_3$. In the search for a simple method of preparation of labeled nitric acid from $N^{15}H_3$, we examined the possibility of direct chemical oxidation of $N^{15}H_3$ to $HN^{15}O_3$. As we know, the majority of oxidizing agents transform ammonia into nitrogen or a mixture of its various oxides [7,8]. We found, however, that under certain conditions $KMnO_4$ oxidizes NH_3 to nitrate in high yield. A study was made of the influence of various factors on the course of this reaction; temperature, pressure, time, concentration and amount of reactants; also the effect of various additives – HCOOH, H_2SO_4, MnO_2 and other substances. The investigations revealed the possibility of realizing a simple method of transformation of $N^{15}H_3$

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* For communications I-III see [1].

to $HN^{15}O_3$, enabling $KN^{15}O_3$ to be obtained in the nitrite-free form in consistently high yields of up to 87-88%.

Salts of nitrous acid-N^{15}, required for the synthesis of N^{15}-labeled compounds, may be prepared by reduction of $KN^{15}O_3$ with lead (yield 64-80% [9, 10]) or with sodium sulfate (yield 50-60% [11]), and also starting from labeled N_2 via N_2O_4, NO and N_2O_3 [5, 6]. We made a fresh study of the method of reduction of potassium nitrate and sodium nitrate with lead, and found that when using 1.5 g-atoms lead per mole nitrate and performing the reaction at 390° in the case of KNO_3 and 330° in that of $NaNO_3$ in vacuum or (better) in an atmosphere of dry nitrogen, the yield of nitrate rises to 91-93%.

Special interest is attached to hydrocyanic acid-C^{14} since this is a key substance widely used for the synthesis of a wide variety of compounds labeled with C^{14}. From 1941 onwards, the literature continuously describes new methods for its preparation*. In spite, however, of the very large number of papers on the synthesis of $HC^{14}N$ published in recent years, the method of preparation that we suggested in 1951 [12] has not only not lost its value but is still the most successful. This method has been the subject of favorable comment by many Russian laboratories and by foreign authors [13].

According to our method, which has been further studied in recent times, the transformation of $BaC^{14}O_3$ into $HC^{14}N$ is realized in a single step by heating the carbonate with metallic potassium and potassium azide in an atmosphere of inert gas. At 350-400° the azide breaks down to nitride, while at 750-780° cyanide is formed. The yield of the latter exceeds 90%. This method is very simple, is characterized by absolute reliability and good reproducibility, and is suitable for preparation of both small and large quantities of $HC^{14}N$.**

The Dutch investigators [13] state that ammonium chloride may be used in place of potassium azide. In our opinion, however, ammonium salts are not to be recommended for this purpose owing to their volatility and the volatility of the potassium amide formed from them. This necessitates working in sealed tubes which complicates the method and lowers its reliability. In comparison with NaN_3 and some other azides, KN_3 has the advantage that its decomposition can be conducted with any desired velocity, since the temperature of this reaction lies above the melting point of KN_3. Decomposition of pure KN_3, however, only takes place at above 500° and goes with extreme violence. Addition to the azide, however, of a small amount of alkali metal facilitates the start of decomposition and the reaction then goes smoothly at 350-400°.

We used $BaC^{14}O_3$ as the source of C^{14}, but potassium or sodium carbonate can also be used with success.

An important factor making possible a high yield of cyanide is the absence of harmful impurities (H_2O, O_2, CO_2) from the inert gas (N_2, H_2, etc.); in this connection it must be noted that N_2 substantially does not participate in the reaction. Another important factor is high purity of the potassium azide: traces of iron lead to formation of Prussian blue, while potassium carbonate leads to dilution of the substance; sulfur-containing impurities are converted under the reaction conditions into sulfides which interfere with the argentometric determination of the cyanide yield. In order to avoid dilution of the active substance, it is necessary to exclude contact of metallic potassium with the carbon dioxide of the air during the synthesis.

Certain difficulties are encountered during the preparation of dry cyanides of the alkali metals from $HC^{14}N$. The evaporation of aqueous [14, 18-20] or methanol [21] solutions of the cyanides, recommended by some authors, leads to serious losses of $HC^{14}N$. The best results are obtained by neutralizing $HC^{14}N$ with potassium or sodium ethoxide in anhydrous alcohol, since cyanides are very poorly soluble in this solvent.

EXPERIMENTAL

1. Preparation of phthalimide-N^{15} and potassium phthalimide-N^{15}. 0.1 mole $N^{15}H_4NO_3$ in the form of a 30-50% solution is charged into a three-necked flask fitted with a Kjeldahl attachment; 40 ml water and 0.105 mole chemically pure, finely crystalline phthalic acid (previously recrystallized from acetic acid and then from water containing carbon) are placed in the receiver. A weak stream of nitrogen is passed through the system, and a small excess of 40% NaOH solution is gradually run in from a dropping funnel. The $N^{15}H_3$ evolved by gentle heating is completely absorbed by the suspension of phthalic acid. Heating is intensified towards the end and about half of the original volume of water is driven off through the air condenser; at the same time the excess of phthalic acid and the ammonium salt formed usually dissolve. Evolution and dis-

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* For a critical review of these methods see, for example, papers [12, 13]; see also papers [14-17] not included in these reviews.

** Another previously described variant of our method [12] consists in heating the previously decomposed potassium azide with barium carbonate; we did not pursue the study of this variant and do not discuss it here.

tillation of the ammonia require 3-4 hours. The solution is transferred to a 300 ml Kjeldahl flask of heat-resistant glass which is connected to a Π-shaped attachment (height 35-40 cm, diameter 12-15 mm), and the water is slowly driven off at a bath temperature (Wood's alloy) of about 140°; during this operation the flask is not more than one-quarter immersed in the bath. After removal of the water, the temperature of the bath is gradually raised. At 180-190° the residue in the flask crystallizes; during the operation a small amount of substance is usually thrown against the walls of the flask, but dehydration commences at about 200° and the partly condensing water washes off the substance adhering to the walls. At 290-300° the whole of the phthalimide formed has sublimed on the walls and in the neck of the flask. Dehydration and sublimation require about 3 hours. The phthalimide is transferred to a small mortar (the residue in the flask is washed out with 15-20 ml water) and triturated with 5% sodium carbonate solution, which is run in dropwise, until alkaline. The precipitate is filtered, washed with 40 ml water and dried in a vacuum-desiccator. Yield 98-99% (about 1% $N^{15}H_3$ is contained in the water driven off during the reaction).

50 ml of hot 2 N solution of potassium ethoxide in anhydrous alcohol is added with shaking to a hot solution of 0.1 mole phthalimide-N^{15} in 350 ml anhydrous alcohol. After cooling, the precipitated phthalimide-N^{15} is filtered, washed with anhydrous alcohol until the filtrate no longer has an alkaline reaction, then washed with acetone and dried in a vacuum-desiccator. The alcoholic mother liquor may be used many times, thereby increasing the yield of potassium phthalimide-N^{15} and making it nearly quantitative.

2. Preparation of $HN^{15}O_3$ and N^{15}-nitrates. 0.82 mole $KMnO_4$ (chem. pure) and 0.15 mole $N^{15}H_3$ in 750 ml water are charged into an autoclave; the mixture is heated 8 hours at 170-180° (the excess of permanganate decomposes completely toward the end of the heating). The MnO_2 is collected and washed with water until the reaction for NO'_3 is negative. The filtrate and wash liquors are combined*, concentrated in vacuum to a volume of 250-300 ml, exactly neutralized with 20% H_2SO_4 and then evaporated to dryness in a dish. The mixture of salts is transferred to a Wurtz flask (with a low sealed-on side-tube), 70 ml H_2SO_4 (d 1.5) is added, and the nitric acid is distilled off on a bath of Wood's metal whose temperature is gradually raised to 230°. The distillate is diluted with water, exactly neutralized with a solution of chemically pure caustic alkali and evaporated to dryness on a water bath. Yield 82-84% of chemically pure nitrate.

3. Preparation of N^{15}-nitrites. 0.01-0.05 mole finely pulverized $KN^{15}O_3$ or $NaN^{15}O_3$ is thoroughly mixed with 0.015-0.075 g-atom lead dust and the mixture is put into a pyrex test tube. The latter is immersed in a bath of Wood's metal so that the level of the mixture is 6-10 mm lower than the level of the alloy, after which the air in the test tube is purged out with nitrogen. The bath is quickly heated to 200° and then brought slowly (after 15-20 min.) to the required temperature. For the preparation of $NaN^{15}O_2$ the mixture is held at 330° for 2 hours, and for that of $KN^{15}O_2$ it is held at 390° for 1 hour. After cooling of the reaction mixture, the nitrite is extracted with 20-50 ml water, and the solution is filtered and evaporated.** If sodium nitrite free from nitrate is required, the residue is recrystallized from water, while the mother liquor is evaporated and the residual substance combined with the next portion of nitrate to be reduced. Due to the repeated reduction of unreacted nitrate, the nitrite can be obtained in nearly quantitative yield.

4. Preparation of $HC^{14}N$ and $KC^{14}N$. The reaction is carried out in a pyrex test tube or flask closed with a stopper through which pass tubes for inflow and discharge of gas. $BaC^{14}O_3$ and KN_3*** are charged into the reaction vessel which is fixed in the sloping position; the air is then driven out with purified and dried nitrogen; metallic potassium is then introduced; the surface of the latter is previously cleaned carefully under a layer of low-boiling ligroine. A gentle nitrogen stream is passed through while the upper part of the mixture is cautiously heated with a burner until the potassium melts; the latter should cover nearly the whole surface of the mixture; the temperature is then raised to maintain a brisk but not violent decomposition of the azide without spattering of the mixture. When decomposition is substantially at an end and the mass has become homogeneous, the vessel is transferred to a furnace. The subsequent conditions of operation and the ratios of components are given in the table.

At the conclusion of the heating, the reaction vessel is withdrawn from the furnace and cooled, in a nitrogen stream, at first in the luminous flame of a burner and then in the air; it is then closed with another stopper to which is attached a dropping funnel (in addition to the nitrogen inlet and exit tubes). Water is cautiously introduced dropwise in the course of 15-45 minutes to the reaction mass which is externally cooled with water; a nitrogen stream is passed through at the same time. The resultant alkaline solution of $KC^{14}N$ is transferred to a flask which is connected to a distillation apparatus (see drawing). 40% H_2SO_4 is run in from the dropping funnel; the solution is boiled in a nitrogen atmosphere for 15-30 minutes while the temperature of the water circulating in the reflux condenser is maintained at about 20°. The $HC^{14}N$ that distills over is absorbed by 2 N caustic alkali solution used in 10% excess. The yield, as determined by titration, is 94-96%; in a blank experiment run under the same conditions, 4-6% HCN is found.

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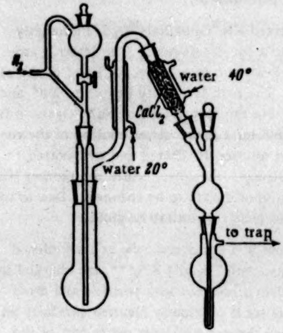
* The HNO_3 content, is determined in an aliquot of the solution with nitron, is 87-88%.

** The yield of nitrite, determined by titration of an aliquot of filtrate with permanganate, is 91-93%.

*** Potassium azide can be prepared by the method described in [22], but a Kjeldahl apparatus must be attached for distillation of HN_3, while only chemically pure KOH must be used for neutralization; the KN_3 solution obtained must be filtered and evaporated in vacuum.

Amounts of components in g			Duration (in min.)	Amount of water (ml)	Amount of 40% H_2SO_4 (ml)	Reaction vessel and type of furnace
$BaC^{14}O_3$	KN_3	K				
0.1	0.2	1.0	2-3	3	5	Test tube 200 x 20; sloping tube furnace
0.2	0.6	1.0	2-3	3	6	Ditto
0.4	1.2	1.2	2-3	5	8	Ditto
0.6	1.2	1.5	2-3	8	10	10 ml Kjeldahl flask; crucible furnace
1.5	3.0	3.0	8	20	30	25 ml Kjeldahl flask; crucible furnace
3.0	6.0	6.0	12	25	60	50 ml Kjeldahl flask; crucible furnace

Notes: 1) Furnace temperature 780-810°. 2) The duration of heating depended to a considerable extent upon the character of the glass from which the reaction vessel was constructed. Thus, if the glass was not "pyrex" but "mazda", the heating had to be prolonged from 3 minutes to 10 minutes.



Distillation apparatus.

If a solid cyanide of an alkali metal is required, the $HC^{14}N$ evolved is passed through a calcium chloride tube heated by a water jacket (water temperature about 40°). The hydrocyanic acid is absorbed in anhydrous alcohol cooled to -25° and $KC^{14}N$ is then precipitated with a solution of C_2H_5OK in anhydrous alcohol.* The yield of $KC^{14}N$ in this case is 80% reckoned on the $BaC^{14}O_3$; the preparation contains 99-100% $KC^{14}N$. The $HC^{14}N$ may also be directly absorbed in the calculated amount of 2 N potassium ethoxide or sodium ethoxide in anhydrous alcohol followed by three times the volume of absolute ether. The yield of $KC^{14}N$ is 85% and the preparation contains 90% cyanide.

SUMMARY

1. Starting from $N^{15}H_3$, methods are developed for the synthesis of phthalimide-N^{15} and of salts of $HN^{15}O_3$ and $HN^{15}O_2$.

2. A one-step method of synthesis of $HC^{14}N$ and its salts from $BaC^{14}O_3$ is developed.

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* 12 ml anhydrous alcohol and 8 ml 2 N potassium ethoxide solution are adequate for the $HC^{14}N$ formed from 3 g $BaC^{14}O_3$.

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Institute of Biological and Medical Chemistry
of the Academy of Medical Sciences, USSR

ALIPHATIC-AROMATIC AMINOALCOHOLS

I. SYNTHESIS OF α-(m-AMINOPHENYL)-β-ALKYLAMINOETHANOLS

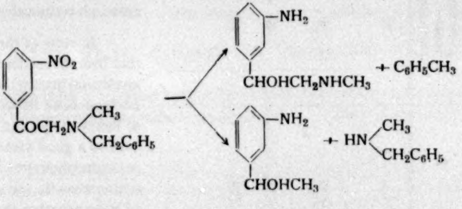
S. I. Sergievskaya and L. E. Sventsitskaya

The objective of the present work was the synthesis of α-(m-aminophenyl)-β-alkylaminoethanols containing different alkyl radicals in the aliphatic amino group: m-$H_2NC_6H_4CH(OH)CH_2NHR$. These compounds have been little investigated, although they are of undoubted interest from the pharmacological aspect. One of us in collaboration with G. A. Ravdel [1] had prepared the dihydrochloride of m-aminophenylmethylaminoethanol; the literature does not report the synthesis of any other m-aminophenylalkylaminoethanols. In the present work we obtained these compounds by reacting m-nitrobromoacetophenone with benzylalkylamines and reducing the resultant m-nitro-ω-benzylalkylaminoacetophenones to m-aminophenylalkylaminoethanols.

The reaction between m-nitrobromoacetophenone and benzylalkylamines was conducted in a medium of anhydrous benzene. m-Nitro-ω-benzylalkylaminoacetophenones were isolated in the form of their hydrochlorides.

Apart from the already known [1] m-nitro-ω-benzylmethylaminoacetophenone, we prepared five compounds of analogous structure (Table 1) which had not previously been described. According to [1] the hydrogenation of m-nitrobenzylmethylaminoacetophenone in presence of Raney nickel at atmospheric pressure and room temperature leads to reduction of only the nitro group, while hydrogenation under the same conditions but in presence of palladium causes the reaction to go right through to the formation of m-aminophenylmethylaminoethanol. We decided to supplement these studies by hydrogenating m-nitrobenzylmethylaminoacetophenone in presence of Raney nickel at higher pressures and temperatures; the completeness of hydrogenation was judged by the amount of hydrogen absorbed and by the absence of a reaction for the carbonyl group in the end product (reaction with Fehling solution).

The best conditions for formation of m-aminophenylmethylaminoethanol were found to be a hydrogen pressure of 35 atm. and a temperature of 75°. Three substances were found in the products of reactions carried out under these conditions: benzylmethylamine, m-aminophenylethanol (m.p. 64-65°) and m-aminophenylmethylaminoethanol (m.p. 84-85°). Formation of these substances showed that hydrogenation goes in two directions under the above conditions:



On the basis of the amount of benzylmethylamine formed (see Experimental), about 30% of the amount of m-nitrobenzylmethylaminoacetophenone hydrochloride taken underwent rupture at the carbon-nitrogen bond in the side chain.

Changes in the conditions of hydrogenation showed that increase of hydrogen pressure to 80 atm. while the

TABLE 1

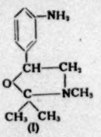
m-Nitro-ω-benzylalkylaminoacetophenones of the general formula $m\text{-}NO_2H_4COCH_2N{<}^{R}_{CH_2C_6H_5}\cdot HCl$

R	Starting components and their amount (g)		Method of purification	Melting point	Yield (%)	Results of analysis (%)					
	m-nitro-ω-bromo-acetophenone	benzylalkylamines $HN{<}^{CH_2C_6H_5}_{R}$				found			calculated		
						C	H	N	C	H	N
$CH(CH_3)_2$	30	36.65	Washing with water and chloroform, recrystallization from alcohol-acetone	155.5—156.5° (with decomp.)	93.9 (not purified)	61.28	5.98	8.12	61.98	6.07	8.03
$(CH_2)_2CH_3$	30	36.65	Washing with acetone, recrystallization from alcohol	164.5 (with decomp.)	76.7 (not purified)	61.98	6.06	8.21	61.98	6.07	8.03
$(CH_2)_3CH_3$	40	53.4	Washing with a mixture of acetone and ether	115—118 (with decomp.)	44.4	62.72	6.45	7.51	62.89	6.39	7.72
$(CH_2)_4CH_3$	15	18.5	Washing with ethyl acetate and recrystallization from alcohol-acetone	138.5—139.5 (with decomp.)	78.2 (not purified)	63.74	6.73	7.44	63.74	6.69	7.43

temperature remained unchanged (75°), has no appreciable influence on the results of the reaction; at lower pressures (8 and 15 atm) and the same temperature (75°) the reaction goes predominantly in the direction of formation of benzylmethylamine and m-aminophenylethanol; hydrogenation does not go to completion, however, at a lower temperature (55°) and a hydrogenation pressure of 35 atm, and the end product contains compounds with a carbonyl group. No new results were obtained by using a weaker nickel catalyst.

m-Aminophenylmethylaminoethanol was isolated for the first time in the form of the base; it is a stable and nicely crystallizing substance, readily soluble in water and distilling in vacuum without decomposition; on the other hand its salts with inorganic acids are not very stable and are hygroscopic, as previously pointed out [1]. The elementary analysis agreed with the composition of this aminoalcohol; in addition we confirmed its structure by a number of reactions.

These reactions included treatment with acetic anhydride which gave the diacetyl derivative $CH_3CONHC_6H_4CH(OCOCH_3)CH_2NHCH_3$; this substance did not give positive reactions for free hydroxyl and aromatic amino groups. The presence of both an amino and hydroxyl group in the side chain was proved by condensation of m-aminophenylmethylaminoethanol with acetone in an alkaline medium* which gave 2,2,3-trimethyl-5-m-aminophenyltetrahydrooxazole (I). Heating of this compound with hydrochloric acid converted it into the original aminoalcohol. The action of acetic anhydride, however, on compound (I) gave the diacetyl derivative of m-aminophenylmethylaminoethanol. These reactions confirmed the structure of 2,2,3-trimethyl-5-m-aminophenyltetrahydrooxazole.


(I)

In view of the fact that hydrogenation of m-nitrobenzylmethylaminoacetophenone in presence of Raney nickel did not lead to a good yield of m-aminophenylmethylaminoethanol, we reverted to the former method of hydrogenation in presence of palladium, but in the light of new data for the properties of m-aminophenylmethylaminoethanol we changed the methods of separation and purification of the compound. By these modifications we obtained m-aminophenylmethylaminoethanol in a yield of 86.2%.

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* Formation of derivatives of tetrahydrooxazole by reaction of aliphatic aminoalcohols with ketones and aldehydes in an alkaline medium is described in the literature [2].

For the preparation of other m-aminophenylalkylaminoethanols (Table 2) we used the same method of hydrogenation of the respective m-nitrobenzylalkylaminoacetophenones in presence of palladium. The method of isolation and purification of these compounds, however, was modified in accordance with the properties of the aminoalcohols formed. The lowest members of this series with alkyl groups C_2H_5 and iso-C_3H_7, similar in physico-chemical properties to m-aminophenylmethylaminoethanol, were prepared in the form of bases and diacetyl derivatives. The bases were isolated by the action of gaseous ammonia on alcoholic solutions of the dihydrochlorides, and were purified by distillation in vacuum.

Aminoalcohols with the radicals C_4H_9 and C_5H_{11} are sparingly soluble in water and form readily crystallizing dihydrochlorides; after hydrogenation, their dihydrochlorides were therefore first separated, and later the aqueous solutions of the latter were treated with 25% aqueous ammonia. In properties, m-aminophenylpropylaminoethanol occupies a position intermediate between the above-mentioned lower and higher homologs; it can therefore be isolated in the form of the dihydrochloride. Separation of this aminoalcohol from its dihydrochloride can be effected either in alcoholic solution with gaseous ammonia or in aqueous solution with the help of aqueous ammonia; a higher yield is obtained, however, in the former case.

EXPERIMENTAL

The starting substances – m-nitroacetophenone and m-nitro-ω-bromoacetophenone – were prepared by the literature methods [3].

Hydrochloride of m-nitro-ω-benzylmethylaminoacetophenone. We considerably simplified the existing method [1] of preparation in respect to isolation and purification of the product. To a suspension of 30.5 g m-nitrobromoacetophenone in 150 ml anhydrous benzene at 15-18° was added dropwise a solution of 30.25 g benzylmethylamine in 30 ml anhydrous benzene. After stirring for 2 hours, 200 ml ether was added and the benzylmethylamine hydrobromide was filtered off (yield 24.1 g; 95.5%). An ethereal solution of hydrogen chloride was added to the filtrate until the reaction was acidic to Congo, and the m-nitro-ω-benzylmethylaminoacetophenone hydrochloride was washed with acetone. Yield 40.1 g (94.5%) with m.p. 173-174° (with decomp.).

Hydrochloride of m-nitro-ω-benzylethylaminoacetophenone. To a solution of 25 g m-nitro-ω-bromoacetophenone in 150 ml anhydrous benzene was added 27.64 g benzylethylamine in 25 ml anhydrous benzene at 6-8°; after the addition, stirring was continued for another 4 hours at the same temperature. The precipitate of benzylethylamine hydrobromide was filtered off; yield 20.5 g (91.4%). The benzene in the filtrate was removed in vacuum and the residual reddish oil dissolved in anhydrous ether (ether was run in until the turbidity disappeared). The ethereal solution was filtered and to the filtrate was added an ethereal solution of hydrogen chloride until acid to Congo. The substance was filtered and washed with a little water and then with chloroform. Yield 18.5 g (54%) substance with m.p. 154-154.5° (with decomp.) after recrystallization from alcohol. The hydrochloride of m-nitro-ω-benzylethylaminoacetophenone is easily soluble in methyl and ethyl alcohols, poorly soluble in acetone, water and chloroform, insoluble in benzene.

Found %: C 61.14; H 5.67; N 8.39. $C_{17}H_{18}N_2O_3 \cdot HCl$. Calculated %: C 60.98; H 5.72; N 8.37.

The remaining hydrochlorides of m-nitrobenzylalkylaminoacetophenones were prepared by the same method as described for m-nitro-benzylethylaminoacetophenone. The data for these compounds are presented in Table 1.

Hydrogenation of the hydrochloride of m-nitro-ω-benzylmethylaminoacetophenone in presence of skeletal nickel catalyst. A solution of 32 g of the hydrochloride of m-nitro-ω-benzylmethylaminoacetophenone in 400 ml methyl alcohol and 10 g skeletal nickel catalyst were placed in a rotating autoclave, hydrogen was pressed in to a pressure of 35 atm. and hydrogenation was carried out at 76°. In the course of two hours the pressure in the autoclave fell to 10 atm., after which the absorption of hydrogen ceased. The catalyst was separated from the reaction mass and the filtrate was acidified with an alcoholic solution of hydrogen chloride until acid to Congo; the methanol was driven off in vacuum on a water bath; traces of moisture in the residual oil were removed by three additions of anhydrous ethanol followed by distillation. A qualitative test with Fehling solution showed the absence of a carbonyl group from the product.

TABLE 2

m-Aminophenylalkylaminoethanols of the general formula: m-$NH_2C_6H_4CH(OH)CH_2NHR$

R	Amounts of substances taken for hydrogenation			Amount of hydrogen absorbed (liters)	Method of separation	Yield (%)	Melting point	Results of analysis (%)					
								found			calculated		
	nitro-amino-ketone (g)	$PdCl_2$ (in g)	ethyl alcohol (in ml)					C	H	N	C	H	N
CH_3	14.0	1.4	96	5.5 (17°, 755 mm)	Action of gaseous ammonia on solution of the hydrogenated product in ethyl alcohol	82.6 (not purified)	84—85°	65.20	8.46	16.86	65.03	8.48	16.84
CH_2CH_3	8.0	0.8	120	3.18 (25°, 748 mm)	Ditto	68.8 (not purified)	80—81	66.58	8.89	15.51	66.63	8.94	15.54
$CH(CH_3)_2$ . . .	12.7	3.0	100	4.7 (20°, 746 mm)	Ditto	53.8 (not purified)	80.5—81.5	68.25	9.24	14.42	68.00	9.34	14.41
$(CH_2)_2CH_3$ . . .	13.0	1.3	100	4.5 (20°, 747 mm)	Ditto	50	74—75	68.00	9.23	14.37	68.00	9.34	14.41
$(CH_2)_3CH_3$ . . .	12.0	1.2	80	4.3 (24°, 760 mm)	Action of 25% aqueous ammonia solution on an aqueous solution of the hydrogenated product followed by extraction with ether	62.4 (not purified)	79.5—80	69.24	9.66	13.53	69.19	9.68	13.45
$(CH_2)_4CH_3$ . . .	6.6	1.5	66	2.32 (22°, 749 mm)	Ditto	74.2 (not purified)	87—88	70.60	9.83	12.49	70.23	9.97	12.60

The product was dissolved in anhydrous ethanol, a stream of gaseous ammonia was passed through the solution, and after addition of ether to complete the precipitation of ammonium chloride, the solution was filtered. The ether and alcohol were driven off from the filtrate and the residue vacuum-distilled. The first fraction with b. p. 70-75° at 7 mm was dissolved in ether and the hydrochloride was separated by the action of an ethereal solution of hydrogen chloride. Nine grams colorless crystals was obtained; m. p. 177-178° after recrystallization from a mixture of alcohol and acetone; no depression of melting point in admixture with a specimen of the hycrochloride of benzylmethylamine. The oil remaining after distillation of the first fraction and weighing 13.3 g was distilled in a vacuum of 0.5 mm. 6.2 g colorless oil came over at 115-155° and trituration with ether led to separation of a solid product with a wide melting range. Fractional crystallization from ether gave two substances. One was α-(m-aminophenyl)-β-methylaminoethanol (2.3 g), colorless crystals with m. p. 84-85°, readily soluble in water, ethanol, methanol and acetone, insoluble in benzene.

Found %: C 65.20; H 8.46; N 16.86. $C_9H_{14}N_2O$. Calculated %: C 65.03; H 8.48; N 16.84.

The second substance (1.5 g) with m. p. 68-69° was α-(m-aminophenyl)-ethanol. *

Found %: C 70.25; H 8.01; N 10.42. $C_8H_{11}NO$. Calculated %: C 70.04; H 8.08; N 10.21.

Hydrogenation of m-nitro-ω-benzylmethylaminoacetophenone hydrochloride in presence of palladium black; α-(m-aminophenyl)-β-methylaminoethanol. 14 g of the hydrochloride of m-nitro-ω-benzylmethylaminoacetophenone, 100 ml ethyl alcohol and a solution of 1.4 g palladium chloride in 5 ml water and 1.4 ml concentrated hydrochloric acid were placed in a hydrogenation bottle. While shaking in a hydrogen atmosphere at 30-35° for 1 hour, 5.5 liters hydrogen (17°, 755 mm) was absorbed. After separation of the catalyst and distillation of the solvents, the residual oil was dissolved in anhydrous ethanol and the base was brought down by passage of gaseous ammonia. Dry ether was added to the solution of the base to completely bring down the ammonium chloride; the liquid was filtered off and the ether and alcohol were driven off in vacuum. A small quantity of dry ether was added to the residue which was seeded with a few crystals of α-(m-aminophenyl)-β-methylaminoethanol. The substance crystallized; yield 6.0 g (82.6%) yellowish crystals with m. p. 83-84°; after recrystallization from anhydrous ethanol the m. p. was 84-85°.

The diacetyl derivative $CH_3CONHC_6H_4CH(OCOCH_3)CH_2NHCH_3$. Acetic anhydride was added dropwise to 0.3 g α-(m-aminophenyl)-β-methylaminoethanol. The resultant oil was triturated with ether to give 0.35 g (77.8%) colorless crystals with poor solubility in alcohol and melting at 152-153°. After recrystallization from ethyl alcohol the m. p. rose to 152.5-153.5°. The compound does not reduce Nessler reagent and gives a negative reaction for the primary aromatic group.

Found %: C 62.67; H 7.22; N 11.13. $C_{13}H_{18}N_2O_3$. Calculated %: C 62.38; H 7.25; N 11.19.

2,2,3-Trimethyl-5-m-aminophenyltetrahydrooxazole (I). 4.7 g α-(m-aminophenyl)-β-methylaminoethanol was dissolved in anhydrous ether and an ethereal solution of hydrogen chloride was added until the reaction was acidic to Congo; the ether was poured off from the resultant oil, the latter was dissolved in 5 ml anhydrous ethyl alcohol, and 25 ml dry acetone was added to the solution. Shaking with excess potassium hydroxide resulted in considerable heat development and the acetone-insoluble oil (the dihydrochloride of the aminoethanol) dissolved completely. The solution was filtered, the acetone and alcohol were driven off from the filtrate, and the residue distilled in vacuum. 4.3 g (74.2%) colorless oil came over at 127-140° and 0.5 mm and soon crystallized. The melting point of the crystals was 83-90° after washing with ether, and 95.5-96.5° after recrystallization from ethyl alcohol. 2,2,3-Trimethyl-5-m-aminophenyltetrahydrooxazole is readily soluble in ethyl alcohol and acetone, very poorly soluble in water and ether.

Found %: C 69.79; H 8.71; N 13.45. $C_{12}H_{18}N_2O$. Calculated %: C 69.86; H 8.78; N 13.58.

Treatment of 0.3 g 2,2,3-trimethyl-5-m-aminophenyltetrahydrooxazole with acetic anhydride followed by trituration of the resultant oil with ether gave 0.3 g (82.4%) colorless crystals with m. p. 151-152°. After recrystallization from ethyl alcohol the m. p. was 152.5-153.5°. A mixed test of the compound with the diacetyl derivative of α-(m-aminophenyl)-β-methylaminoethanol did not give a depression of melting point.

Two grams 2,2,3-trimethyl-5-m-aminophenyltetrahydrooxazole was heated for 3 hours with 40 ml 15% solution of hydrogen chloride in ethyl alcohol; one half of the ethyl alcohol was distilled off and gaseous ammonia was passed through the residual alcoholic solution, followed by addition of 60 ml dry ether; the ammonium chloride

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* The literature reports m. p. 68-69°.

was filtered off. The ether and alcohol were driven off from the filtrate and the residual oil was triturated with a little dry ether and a few crystals of α-(m-aminophenyl)-β-methylaminoethanol. The resultant colorless crystals melted at 83-84°. No depression was observed in a mixed test with α-(m-aminophenyl)-β-methylaminoethanol obtained by another route. The yield of α-(m-aminophenyl)-β-methylaminoethanol was 1.2 g (75.1%).

α-(m-Aminophenyl)-β-(n-butyl)-aminoethanol. 1.2 g palladium chloride in 5 ml water and 1.5 ml hydrochloric acid were added to a solution of 12 g of the hydrochloride of m-nitro-ω-benzyl-(n-butyl)-aminoacetophenone in 80 ml ethyl alcohol; hydrogenation was effected at 30-35°; after 2 hours, 4.3 liters hydrogen (24°, 760 mm) had been absorbed; the theoretical amount of hydrogen under these conditions is 4.45 liters. The catalyst was separated from the reaction mass and the alcohol, water and toluene were distilled off; colorless crystals came down and after washing with alcohol had m. p. 208-210° (with decomp.). A test with Fehling solution showed the absence of a carbonyl group. The product had m. p. 212-213° (with decomp.) after recrystallization from a mixture of alcohol and ether. The dihydrochloride of α-(m-aminophenyl)-β-(n-butyl)-aminoethanol forms colorless crystals, rapidly turning pink in the air, readily soluble in water, less soluble in ethyl alcohol, insoluble in acetone, ether and benzene.

Found %: N 9.95; Cl 25.39. $C_{12}H_{20}N_2O \cdot 2HCl$. Calculated %: N 9.96; Cl 25.22.

The dihydrochloride of α-(m-aminophenyl)-β-(n-butyl)-aminoethanol was dissolved in 5 ml water and a 25% ammonia solution was added to it until strongly alkaline; the resultant yellow oil was extracted with ether. The extract was dried with sodium sulfate, and part of the ether was then driven off. Crystallization from ether gave 3.4 g substance with m. p. 78.5-79.5°. A further 0.9 g substance with m. p. 77-78° was recovered from the mother liquor. Total yield 62.41%. After recrystallization from acetone the m. p. was 79.5-80°. α-(m-Aminophenyl)-β-(n-butyl)-aminoethanol forms colorless crystals, readily soluble in alcohol, poorly soluble in acetone and ether, insoluble in water and benzene.

Found %: C 69.24; H 9.66; N 13.53. $C_{12}H_{20}N_2O$. Calculated %: C 69.19; H 9.68; N 13.45.

m-Aminophenylalkylaminoethanols in which the alkyl group was C_2H_5 or iso-C_3H_7 and their diacetyl derivatives were prepared by the method described for m-aminophenylmethylaminoethanol and its diacetyl derivative. m-Aminophenylalkylaminoethanols in which the alkyl is n-C_3H_7, n-C_4H_9 and n-C_5H_{11} and their dihydrochlorides were prepared by exactly the same method as for m-aminophenylbutylaminoethanol and its dihydrochloride. Some data for m-aminophenylalkylaminoethanols and their derivatives are presented in Tables 2, 3 and 4.

TABLE 3

Diacetyl Derivatives of m-Aminophenylalkylaminoethanols of the General Formula m-$CH_3CONHC_6H_4CH(OCOCH_3)CH_2NHR$

R	Yield (%)	Melting point	Results of analysis (%)					
			found			calculated		
			C	H	N	C	H	N
CH_3	77.8	152.5—153.5°	62.67	7.22	11.13	62.38	7.25	11.19
CH_2CH_3	95.9	133—133.5	63.54	7.52	10.54	63.61	7.63	10.60
$CH(CH_3)_2$	83.8	136—136.5	64.84	7.84	10.06	64.72	7.96	10.06

TABLE 4

Dihydrochlorides of m-Aminophenylalkylaminoethanols of the General Formula m-$NH_2C_6H_4CHOHCH_2NHR \cdot 2HCl$

R	Melting point	Results of analysis (%)					
		found			calculated		
		C	H	N	C	H	N
$(CH_2)_2CH_3$	203—204° with decomp.	49.58	7.53	10.51	49.44	7.54	10.48
$(CH_2)_3CH_3$	212—213 with decomp.	—	—	9.95	—	—	9.96
$(CH_2)_4CH_3$	227—228 with decomp.	52.78	7.96	9.50	52.88	8.19	9.49

SUMMARY

1. m-Nitro-ω-benzylalkylaminoacetophenones containing the radicals C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9 and n-C_5H_{11} were prepared. These are not described in the literature.

2. The hydrogenation of m-nitro-ω-benzylmethylaminoacetophenone at high pressure and elevated temperature in presence of Raney nickel was investigated.

3. m-Aminophenylmethylaminoethanol was condensed with acetone in an alkaline medium to give 2,2,3-trimethyl-5-m-aminophenyltetrahydrooxazole.

4. α-(m-Aminophenyl)-β-alkylaminoethanols (not previously described) and some of their derivatives were prepared.

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S. Ordzhonikidze Institute of Pharmaceutical Research Received July 26, 1955.

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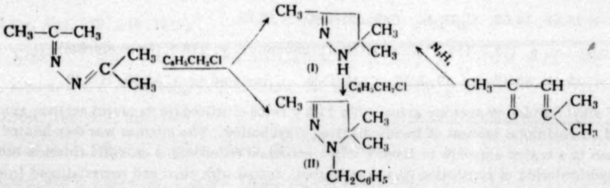
REACTIONS OF HYDRAZINE DERIVATIVES

VI. THE ACTION OF ALKYL HALIDES ON ACETONE AZINE

A. N. Kost, G. A. Golubeva and I. I. Grandberg

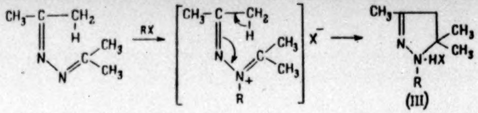
In 1899 Franke [1] reacted isobutyraldehyde azine with ethyl iodide and obtained a compound whose composition he failed to elucidate. Thiele [2] later found that dimethyl sulfate smoothly adds on to benzaldehyde azine to give a product from which methylhydrazine was formed on hydrolysis. This reaction does not go, however, even with diethyl sulfate. Thiele also reacted acetone azine with ethyl iodide and obtained a mixture of substances which were not closely investigated.

In an investigation of the products of reaction of acetone azine with benzyl chloride, we isolated a substance which was identified as the hydrochloride of 3,5,5-trimethylpyrazoline (crystallizing from the reaction mass); hydrolysis, alkalization and distillation of the residual products gave the free 3,5,5-trimethylpyrazoline (I) and 3,5,5-trimethyl-1-benzylpyrazoline (II). 3,5,5-Trimethylpyrazoline (I) proved to be identical with the substance obtained by N. M. Kizhner [3] by the action of hydrazine on mesityl oxide, as was confirmed by a mixed melting point test of the hydrochlorides and picrates. Treatment of the authentic pyrazoline (I) with benzyl chloride gave the pyrazoline (II) which was identical with that obtained by rearrangement.



Methyl iodide (likewise dimethyl sulfate) undergoes an intensely exothermic reaction with acetone azine. Other alkyl halides react slowly at room temperature, but the reaction goes in 1-2 hours on heating (50-80°). The reaction goes more slowly with alkyl iodides than with the corresponding bromides.

It may be suggested that the alkyl halide hydrolyzes in presence of traces of moisture to form hydrogen halide, and the latter promotes cyclization of the azine. We previously described some cases of this reaction in presence of oxalic or formic acid [4]. It was found that the hydrochloride of pyrazoline (I) actually promotes cyclization of the azine but only after prolonged heating. With alkyl halides, however, cyclization of the azine goes both in an aqueous medium and in the absence of moisture, and in some cases with spontaneous heating. At first the alkyl halide apparently adds on to acetone azine (as in the case with benzaldehyde azine) and then, due to shifting of the electronic density, the mobility of the α-hydrogen atom is increased, thus facilitating formation of the cyclic system.



The resultant salt of N-alkylpyrazoline effects further isomerization of the azine, and the free non-alkylated base (I) is formed. With rise of temperature, alkylation of the already formed pyrazoline (I) is observed.

EXPERIMENTAL

3,5,5-Trimethylpyrazoline (I) was prepared by cautious mixing of 133 g mesityl oxide with 70 g hydrazine hydrate [3]. Treatment with solid alkali, extraction with ether, drying with alkali and two distillations gave 126 g (82%) 3,5,5-trimethylpyrazoline with b. p. 62° (21 mm), n_D^{20} 1.4573. Picrate, m. p. 137.5° (from alcohol); hydrochloride, m. p. 171° (from alcohol). Literature data: b. p. 63-64° (23 mm) [5]; 66-69° (20 mm) [6], n_D^{20} 1.4515 [7], 1.4566 [3]; picrate, m. p. 138° [7]; hydrochloride, m. p. 170° [6], 176° [5].

The same pyrazoline [b. p. 62-64° (22 mm), n_D^{20} 1.4563, hydrochloride with m. p. 171-172° (from alcohol) does not give a depression in admixture with the preceding product] is obtained by heating acetone azine and 0.7 g of the hydrochloride of pyrazoline (I) for 2 hours on a water bath. Hydrolysis of the reaction mass by boiling with 150 ml 2 N hydrochloric acid (under these conditions the azine is quantitatively cleaved), evaporation to half the volume (for removal of the acetone formed and of the products of its autoxidation), alkalization, extraction with ether and distillation gave 5.5 g (49%) of the pyrazoline (I).

Reaction of 14.2 g methyl iodide with 11.2 g pyrazoline (I) (spontaneous heating, then 24 hours at room temperature) gave a crystalline mass of the hydroiodide of 1,3,5,5-tetramethylpyrazoline (III). After four recrystallizations from alcohol the yield was 53%, m. p. 154°, in agreement with the literature [7].

Similarly, reaction of 11.2 g pyrazoline (I) with 12.6 g benzyl chloride, followed by decomposition with alkali and distillation, gave 2.8 g original pyrazoline (I) and 6 g (30%) 1-benzyl-3,5,5-trimethylpyrazoline (II) with b. p. 168-171° (52 mm), n_D^{20} 1.5294, d_4^{20} 0.9922, MR_D 62.92, calc. 62.68.

Found %: N 13.98, 14.08. $C_{13}H_{18}N_2$. Calculated %: N 13.85.

Hydrochloride, m. p. 153.5-154.5° (from alcohol); picrate, m. p. 178.5° (from alcohol).

Found %: C 53.09, 53.17; H 5.17, 5.17. $C_{19}H_{22}O_7N_5$. Calculated %: C 53.08; H 5.12.

Action of alkyl halides on acetone azine. To 11.2 g twice-distilled (in vacuum) acetone azine [4] was gradually added an equimolar amount of freshly distilled alkyl halide. The mixture was then heated on a water bath for 1-2 hours in a sealed ampoule or under a reflux condenser fitted with a calcuim chloride tube. The precipitate of hydrochloride of pyrazoline (I) was separated, washed with ether and recrystallized from alcohol. The residual reaction mass was hydrolyzed by boiling for 2-3 hours with 100-150 ml 2 N hydrochloric acid [in order to decompose the unreacted azine whose boiling point is close to that of pyrazoline (I)], making strongly alkaline and extracting with ether. The ethereal extracts were dried with potassium carbonate; the ether was driven off, and the residue fractionated several times in vacuum.

In this manner 22.4 g azine and 27.5 g butyl bromide (46 hours in ampoule, 90-100°) gave traces of pyrazoline (I) and 13 g (38.7%) 3,5,5-trimethyl-1-butylpyrazoline with b. p. 70° (6 mm), n_D^{20} 1.4551, d_4^{20} 0.8664, MR_D 52.60; calc. 52.43.

Found %: C 71.46, 71.51. H 11.83, 11.85. $C_{10}H_{20}N_2$. Calculated %: C 71.37; H 11.98.

Picrate, m. p. 118-120° (after three recrystallizations from alcohol).

Found %: N 17.34, 17.52. $C_{16}H_{23}O_7N_5$. Calculated %: N 17.66.

11.2 g acetone azine and 12.1 g allyl bromide were reacted 1-2 hours at room temperature to give a precipitate of 5.2 g of the hydrobromide of pyrazoline (I) with m. p. 170° (after two recrystallizations from alcohol). (Literature data: m. p. 170° [8]). The residual mass was heated 1 hour on a water bath and after the usual treatment gave 2 g pyrazoline (I) with b. p.65-69° (19 mm), n_D^{20} 1.4571; picrate, m. p. 134.5°. Total yield 46% (including the previously isolated hydrobromide). In addition 2.8 g (18%)of 3,5,5-trimethyl-1-allylpyrazoline was obtained; b. p. 77-80° (19 mm), n_D^{20} 1.4676, d_4^{20} 0.8957, MR_D 47.20 (calc. 46.93). Picrate, m. p. 86-87° (after three recrystallizations from alcohol).

Found %: N 18.24, 18.34. $C_{15}H_{19}O_7N_5$. Calculated %: N 18.27.

In a similar experiment with allyl chloride, 1 g of the hydrochloride of pyrazoline (I) was isolated [m. p. 171-172° (from alcohol) no depression in a mixed melting test with an authentic specimen]; other products were a) 5 g of the free pyrazoline (I) total yield 51% with b. p. 55-57° (13 mm), n_D^{20} 1.4560, m. p. of hydrochloride 171°; and b) 2.9 g (19%) 3,5,5-trimethyl-1-allylpyrazoline with b. p. 78-79° (18 mm), n_D^{20} 1.4676; picrate, m. p. 86-87°.

Heating of benzyl chloride (12.6 g) with acetone azine (11.2 g) for 2 hours on a water bath gave 5 g of the hydrochloride of pyrazoline (I) with m. p. 170-171° (no depression in admixture with the pure substance), 2.8 g of the free pyrazoline (I) [total yield 59%; picrate, m. p. 137°], and 6.1 g (30 %) 3,5,5-trimethyl-1-benzylpyrazoline (II) with b. p. 134-135° (8 mm), n_D^{20} 1.5301, d_4^{20} 0.9922, m. p. of hydrochloride 153.5-154.5° (after recrystallization from alcohol), m. p. of picrate 179° (after three recrystallizations from alcohol); no depression of melting point in a mixed test with the picrate of the above-described picrate of pyrazoline (II). A similar experiment with benzyl bromide gave the hydrobromide of pyrazoline (I) with m. p. 169-170° and pyrazoline (II) with b. p. 133-134° (7 mm), n_D^{20} 1.5299; picrate, m. p. 178-179°.

SUMMARY

Under the action of alkyl halides, acetone azine undergoes rearrangement with formation of 3,5,5-trimethylpyrazoline and 3,5,5-trimethyl-1-alkylpyrazoline. The ratio of the reaction products depends upon the activity of the halide, the structure of the alkyl radical and the conditions of the reaction.

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Moscow State University.

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THE CHANGE OF THE CHEMICAL HETEROGENEITY OF CELLULOSE XANTHATE DURING THE RIPENING OF VISCOSE

A. T. Serkov, A. B. Pakshver and E. M. Mogilevsky

The heterogeneity of cellulose xanthate as reflected in the degree of esterification was demonstrated by a number of investigators [1-3]. In view of the instability of cellulose xanthate and the fact that an equilibrium is established in reaction (1)

$$\text{Cell.}-\text{OH} + \text{CS}_2 + \text{NaOH} \rightleftharpoons \text{Cell.}-\text{O}-\text{CSSNa} + \text{H}_2\text{O}, \qquad (1)$$

it may be suggested that solution of xanthate in viscose is followed by transesterification of the hydroxyls of cellulose, due to which the heterogeneity of the xanthate, as regards esterification, will be evened out. The possibility of transesterification reaction, i. e. passage of the dithiocarbonate group from one hydroxyl of cellulose to another hydroxyl, is assumed by many authors. Centola [4] observed supplementary solution of cellulose in viscose and attributed this phenomenon to a transesterification reaction. Cellulose freshly introduced into the viscose is xanthated by the carbon disulfide which is always present in accordance with equation (1). However, the solubility of cellulose in viscose may be accounted for by the fact [5] that cellulose is soluble to a certain extent in a 6-8% solution of sodium hydroxide. Reference has also been made to the possibility of transesterification and disappearance of the chemical heterogeneity of the xanthate during solution and ripening of viscose [6]. The existing experimental data, however, do not permit a decisive conclusion as to the possibility of transesterification of cellulose xanthate and of the diminution of its chemical heterogeneity. In our experiments (see Table) data were obtained which permit a direct answer to this question. The viscose used in the investigation was prepared both by "wet" xanthation and by the usual procedure. The first fractionation was effected immediately after solution, and the second after ripening for 16 hours.

The following fractionation procedure was adopted.

Twenty grams viscose was put into a graduated flask of 250 ml capacity which was then filled up to the mark with 4% sodium hydroxide solution. Two samples were withdrawn: one of 25 ml for determination of the degree of esterification by the known method [2]; the other of 100 ml for fractionation. Both samples were neutralized with 1 N acetic acid solution (phenolphthalein test) and treated with diethyl chloroacetamide (first sample 1 ml, the second 4 ml). The precipitated diethyl chloroacetamide derivative of cellulose xanthate was washed with methanol and then with ether. The first precipitate (from the 25 ml) was dried at 50°, weighed and analyzed for nitrogen by the Kjeldahl method; in this manner the γ_{CS_2} of the original xanthate could be calculated. The second sample was dissolved in 100 ml 70% aqueous solution of ethylene chlorohydrin. Solution was facilitated by first triturating the xanthate derivative thoroughly in a mortar in the dry form and then with the amount of water that should be present in the solution (30 ml); the suspension was then transferred to a bottle with a ground-glass stopper and 70 g ethylene chlorohydrin added in small portions while stirring. Solution was then effected by shaking for one hour. A small amount of water wad added dropwise to the resultant solution with vigorous stirring until cloudy. The next day the precipitate was centrifuged, washed with a small quantity of water (5 ml), with methanol, and with ether, dried at 50° to constant weight, weighed, and transferred to a flask for Kjeldahl determination of nitrogen.

The degree of esterification is calculated from the formula:

$$\gamma CS_2 = \frac{1.62 \cdot n}{m - 0.0189 \cdot n},$$

where n is the amount of 0.1 N HCl solution (in ml) used in titration of the ammonia, and m is the weight of the sample of derivative (in g).

Composition of Fractions of Cellulose Xanthate Obtained in Xanthating Cylinder and by Emulsion Xanthation

Fraction number	Xanthation in cylinder				Emulsion xanthation			
	immediately after solution		after 16-hours' ripening		immediately after solution		after 16-hours' ripening	
	wt. of fraction (g)	γCS_2	wt. of fraction (g)	γCS_2	wt. of fraction (g)	γCS_2	wt. of fraction (g)	γCS_2
Mean value of γCS_2	–	45.2	–	37.3	–	51.0	–	40.6
Weight of total sample	1.0392	–	1.0024	–	1.0200	–	1.0048	–
First fraction	0.5684	40.1	0.1256	36.5	0.0630	39.4	0.1918	41.2
Second fraction	0.0964	50.4	0.3010	37.8	0.5571	49.6	0.5674	40.2
Third fraction	0.3744	53.8	0.5755	37.2	0.3999	55.4	0.2462	41.4

The second fraction is isolated by addition of excess of water (100 ml including the 5 ml taken for washing the first fraction). The degree of esterification and the weight of the third fraction are determined by difference, knowing the degree of esterification of the original derivative and its weight.

We see from the experimental data in the Table that the xanthate is extremely heterogeneous in its degree of esterification immediately after solution. This heterogeneity is governed by the structure of the cellulose, by the presence of individual portions with different degrees of molecular regularity and of orientation of the macromolecules, as well as by technological factors. Ripening of viscose is accompanied by transesterification of the hydroxyls of the cellulose, and since the influence of the structure of the fiber becomes less important in solution, the process of transesterification leads to the degree of esterification of the xanthate becoming more uniform throughout. After 16 hours' ripening of the viscose, it was impossible to isolate from any of the samples a fraction whose γ_{CS_2} differed appreciably from that of the other fractions.

We can accordingly assume that an equilibrium expressed by equation (1) is established in viscose. If we accept the theory of Meos [7] and other authors [8] that during xanthation the carbon disulfide only reacts after transition to dithiocarbonate, the mechanism of cellulose xanthation may be represented by the following scheme:

$$CS_2 + NaOH \rightleftharpoons NaHCS_2O, \tag{2}$$

$$\text{Cell.} -OH + NaHCS_2O \rightleftharpoons \text{Cell.} -OCS_2Na + H_2O. \tag{3}$$

The following mechanism of transesterification may be proposed: The xanthated groups split off in the form of dithiocarbonate which can again react with the free hydroxyls of the cellulose to form xanthate groups; the cellulose xanthate thus becomes uniformly esterified. Part of the dithiocarbonate, however, reacts with alkali to form Na_2S and Na_2CS_3 and is therby removed from the sphere of reaction.

SUMMARY

1. Cellulose xanthate obtained by the usual technique (barrel xanthation) and by the technique of "wet" xanthation is extremely heterogeneous in respect of degree of esterification.

2. The chemical heterogeneity of cellulose xanthate gradually disappears during the ripening of viscose. The levelling-out of the degree of esterification is accounted for by a process of transesterification of the hydroxyls of the cellulose in the viscose solution.

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All-Union Institute of Artificial Fiber Research.

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SUMMARY

1. Cellulose xanthate obtained by the usual technique [illegible] in the case of "low" xanthation, a xanthate is [illegible] in respect of degree of esterification.

2. The chemical heterogeneity of cellulose xanthate [illegible] the leveling-out of the degree of esterification is accelerated [illegible] of the cellulose in the course of ripening.

[1] S. N. Danilov and [illegible]

[2] [illegible]

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[7] A. I. [illegible] Exchange of [illegible]

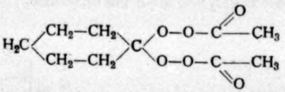
[8] H. [illegible]

Institute of Artificial Fiber Research [illegible]

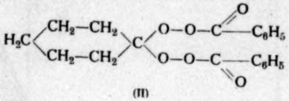
THE CHAIN REACTION OF CARBON TETRACHLORIDE WITH ISOPROPYL ALCOHOL INITIATED BY ACETYLATED AND BENZOYLATED HYDROPEROXIDES OF 1-HYDROXYCYCLOHEXANONE

G. A. Kolpovskaya, B. N. Moryganov, G. A. Razuvaev and V. A. Shushunov

It was earlier established [1] that radicals formed by thermal decomposition of benzoyl peroxide initiate a chain reaction of carbon tetrachloride with methyl and isopropyl alcohols. The present communication gives the results of investigation of the reaction of carbon tetrachloride with isopropyl alcohol initiated by acetylated (I) and benzoylated (II) hydroperoxides



(I)



(II)

of 1-hydroxycyclohexanone. A comparison can be made of the activity of $CH_3COO^{\cdot}$ and $C_6H_5COO^{\cdot}$ radicals formed by thermal breakdown of the above hydroperoxides.

The chief end products of the reaction that we investigated are HCl, acetone and chloroform. We quantitatively determined the first two substances but the chloroform was only qualitatively detected. Since the concentrations of hydroperoxides in our solutions were small, we usually did not study the quantitative ratio of the products formed by decomposition of the initiators.

The mechanism of a similar chain reaction has already been considered [1]; in the present work we therefore limited ourselves to quantitative determination of the main reaction products after a period of time long enough for complete decomposition of the hydroperoxides; we also studied the kinetics of the process.

Our preliminary experiments showed that initiation of the reaction between CCL_4 and $CH_3CHOHCH_3$ takes place even at 40-50° and with a concentration of hydroperoxide of the order of several thousandths of a mole per liter of mixture. The reaction velocity increases sharply with rising temperature. At a temperature of about 80° both the acetylated and the benzoylated hydroperoxides of 1-hydroxycyclohexanone were completely decomposed after 40-50 hours in the mixtures that we investigated. The Table shows the results of quantitative determination of some of the main products of the reaction. These results very convincingly demonstrate the occurrence of a chain reaction in the mixture under investigation.

It is usual to characterize chain reactions by the length of chain of one of the products of reaction. Chain length may depend, however, on many factors (temperature, composition of reaction mixture, concentration of added substances, etc.). Furthermore, the reaction products (whose concentration may govern the chain length) may themselves undergo further chemical changes.

Concentration of hydroperoxides $C \cdot 10^2$ (moles/liter)	No. of moles of substances formed per mole of decomposed hydroperoxide		
	HCl	CH_3COCH_3	CO_2
	Acetylated hydroperoxide		
0.63	26.0	20.6	0.57
	25.6	20.9	0.53
2.5	9.8	9.0	0.17
	9.4	8.6	0.18
7.5	2.8	2.6	0.05
	3.1	2.9	0.05
	Benzoylated hydroperoxide		
0.27	59.0	38.9	—
	64.0	38.8	1.5
1.1	24.5	13.0	0.76
	25.0	14.0	0.83
3.3	9.8	6.5	0.39
	10.3	7.4	0.40

In Fig. 1 the length of chain (with respect to HCl) is plotted as a function of the initial concentration of hydroperoxide when the reaction mixture has been heated until the initiator has been decomposed. As we see from Curve 2, the chain length increases sharply with falling concentration of hydroperoxide below 0.01 mole/liter and is relatively little dependent upon the content of hydroperoxide in more concentrated solutions. The same diagram also reveals that the chain length (with respect to HCl) for the reaction initiated by the acetylated hydroperoxide is considerably smaller than for the same reaction initiated by benzoylated hydroperoxide. This difference in chain length (with respect to HCl) may be due to the fact that the ratio of the velocity of radical decomposition of hydroperoxide to the velocity of its reaction with the alcohol in the "cell" is not the same for the two initiators used in this work. The ratio is smaller for acetylated hydroperoxide than for benzoylated hydroperoxide, as the Table shows. The chain length with respect to acetone is considerably greater for the reaction initiated by acetylated hydroperoxide than for that initiated by benzoylated hydroperoxide. The chain length with respect to CO_2 also shows this difference.

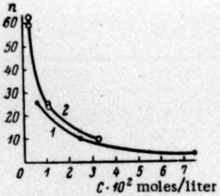


Fig. 1. Chain length (n) with respect to HCl as a function of the concentration of hydroperoxide. 1) with acetylated hydroperoxide; 2) with benzolated hydroperoxide of 1-hydroxycyclohexanone.

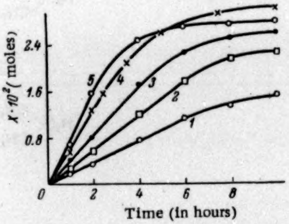


Fig. 2. Rise of concentration of HCl in the reaction mixture in course of the reaction. 1,2,3,4 and 5 were plotted with respective initial concentrations of acetylated hydroperoxide of $5 \cdot 10^{-3}$, $1.5 \cdot 10^{-2}$, $2.5 \cdot 10^{-2}$, $5 \cdot 10^{-2}$ and $7.5 \cdot 10^{-2}$ moles/liter.

We studied the kinetics of formation of HCl in the reaction of carbon tetrachloride with isopropyl alcohol initiated by acetylated hydroperoxide. Several kinetic curves, plotted at 55° (Fig. 2) with various concentrations of hydroperoxide, show the reaction course. From the slope of the initial rectilinear portion of these kinetic curves, we can evaluate the rate of development of the chemical processes in the investigated mixture of liquid substances. The abscissas in this diagram represent the duration of reaction, and the ordinates the number of moles of HCl (X) formed by reaction of 1 mole of mixture (0.5 mole CCl_4 and 0.5 mole $CH_3CHOHCH_3$).

In Fig. 3 the Curve drawn through the experimental points represents the dependence of the initial reaction velocity (W_0) on the concentration of hydroperoxide. The ordinates represent the initial velocity $W_0 = X \cdot 10^3$ moles/hour; the abscissas represent the concentration of acetylated hydroperoxide. We see that the initial velocity of formation of HCl rises linearly with the concentration of hydroperoxide when the latter exceeds 0.02 mole/liter.

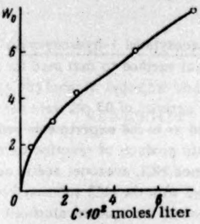


Fig. 3. Influence of concentration of acetylated hydroperoxide on the initial velocity of formation of HCl at 55°.

At lower concentrations of hydroperoxide, this dependence is not observed and additions of hydroperoxide have a greater influence on the velocity of the reaction.

We also made a fairly close study of the influence of temperature on the initial velocity of evolution of HCl. Results of these experiments are plotted in Fig. 4. All these experiments were carried out with a constant initial concentration of hydroperoxide of $5 \cdot 10^{-2}$ mole/liter. A very strong dependence on temperature is observed.

From the initial straight-line portions of the kinetic curves plotted in Fig. 4, the reaction velocity (W_0) was determined for the experiments performed at the different temperatures; on this basis the dependence of log W_0 on the reciprocal of the temperature was plotted in Fig. 5. The experimental points on this graph are closely distributed about the straight line drawn through them. This demonstrates the applicability of the Arrenhius law to the reaction under the given experimental conditions. From the slope of the straight line we determined the energy of activation and obtained a value of 25.8 ± 0.5 kcal/mol.

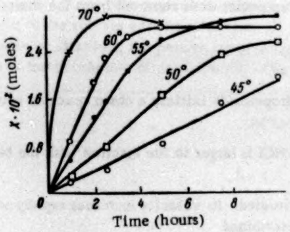


Fig. 4. Rise of concentration of HCl in the reaction mixture during reaction at various temperatures.

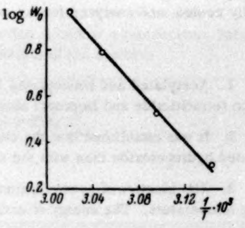


Fig. 5. Rate of formation of HCl as a function of temperature.

EXPERIMENTAL

Chain reaction of carbon tetrachloride with isopropyl alcohol initiated by benzoylated 1-hydroxycyclohexanone hydroperoxide. The benzoylated derivative was synthesized from cyclohexanone hydroperoxide and benzoyl chloride [2]. The benzoylated hydroperoxide used in the experiments had an activity of 67.5% (in calculating the yields of HCl, acetone and CO_2, conversion was made to a 100% basis). The reaction mixture, comprising equimolar amounts of carbon tetrachloride (154 g) and isopropyl alcohol (60 g) and varying amounts of benzoylated hydroperoxide (0.25, 1 and 3 g), was charged into a flask fitted with a reflux condenser (ground-glass connection) and connected to absorption vessels; the flask was heated on a water bath for 54 hours.

The gaseous products of reaction were absorbed – the HCl in distilled water and the CO_2 in saturated barium hydroxide solution. The CO_2 was determined gravimetrically. The mixture of liquid reaction products were washed to neutrality with distilled water to remove acetone and HCl as well as unreacted alcohol and other water-soluble substances. The aqueous alcoholic solution was combined with HCl solution from the absorbers. The HCl in the mixture was gravimetrically determined as AgCl, and the acetone was determined in the form of the 2,4-dinitrophenylhydrazone. After washing with water and drying with $CaCl_2$, the liquid, water-insoluble reaction products were fractionally distilled. A fraction with b. p. 59-76° (mixture of chloroform and carbon tetrachloride) was taken off. After further drying with $CaCl_2$ and then with P_2O_5, this fraction was again fractionated in a column to give a chloroform fraction with b. p. 60-62° (d_4^{20} 1.4759, n_D^{20} 1.4427). Material from several experiments was combined for the fractionations. The residue after distillation of the 59-76° fraction was made alkaline and steam-distilled. The non-distillable portion was freed from resin and acidified with dilute hydrochloric acid; benzoic acid was thus isolated. o-Phthalic acid was detected in the resin by the fluorescein test with resorcinol.

Chain reaction of carbon tetrachloride with isopropyl alcohol initiated by acetylated 1-hydroxycyclohexanone hydroperoxide. The acetylated hydroperoxide was prepared by a similar method to that used for the benzoylated derivative [2]. Equimolar amounts of carbon tetrachloride (154 g) and isopropyl alcohol (60 g) and various amounts of acetylated hydroperoxide (0.25, 1, and 3 grams) with an activity of 97.4% were heated on a water bath for 40 hours. The gases formed during the reaction were absorbed as in the experiments with benzoylated hydroperoxide. The CO_2 was determined gravimetrically. The liquid products of reaction were washed to neutrality with distilled water. The aqueous alcoholic solution contained HCl, acetone, acetic acid, unreacted alcohol and other water-soluble substances. The solution was combined with the HCl solution from the absorbers and analyzed as before for its content of HCl and acetone. A portion of the aqueous alcoholic solution was neutralized with 0.1 N NaOH solution and evaporated down. The dry residue was examined for acetic acid which was detected by the cacodyl reaction. The liquid, water-insoluble products were dried with $CaCl_2$ and fractionally distilled. A first 50-60° fraction was further dried with $CaCl_2$ and then with P_2O_5 before refractionation in a column to give a chloroform fraction with b. p. 61-65° (d_4^{20} 1.4702, n_D^{20} 1.4410).

Kinetics of the chain reaction of carbon tetrachloride with isopropyl alcohol initiated by acetylated 1-hydroxycyclohexanone hydroperoxide. A reaction mixture consisting of equimolar amounts of carbon tetrachloride (12.02 ml) and isopropyl alcohol (9.5 ml) and various amounts of acetylated hydroperoxide was charged into ampoules (volume about 25 ml). The ampoules were sealed and placed in a thermostat whose temperature was kept constant to within ± 0.1°. At definite time intervals the ampoules were removed from the thermostat, rapidly cooled, and analyzed for the amount of HCl formed.

SUMMARY

1. Acetylated and benzoylated 1-hydroxycyclohexanone hydroperoxide initiate a chain reaction between carbon tetrachloride and isopropyl alcohol.

2. It was established that the chain length with reference to HCl is larger in the reaction with the benzoylated hydroperoxide than with the acetylated derivative.

3. The kinetics of accumulation of HCl in the reaction was studied. Its velocity increases rapidly with rising temperature. The energy of activation of this process was determined.

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Gorky State University

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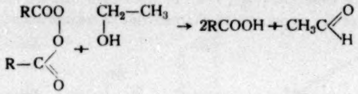
*T. p. = C. B. Translation pagination.

REACTIONS OF ACETYL BENZOYL PEROXIDE WITH ALCOHOLS AND ACETIC ACID

G. A. Razuvaev and V. N. Latyaeva

The thermal decomposition of symmetrical acetyl and benzoyl peroxides in alcohols and acids has interested many authors. Kharasch, Rowe and Urry proposed a free-radical mechanism of decomposition of acetyl peroxide in n-butyl, isobutyl, sec-butyl, isopropyl and tert-butyl alcohols [1]. The main products of the reaction were methane, CO_2, acetic acid, methyl acetate, acetic esters of the solvent, aldehydes or ketones. The products of reaction with deuterated alcohols indicated that dehydrogenation of the alcohol occurred at the α-carbon atom. Kh. S. Bagdasaryan and R. I. Milyutinskaya [2] believed that the initial reaction of breakdown to radicals does not depend upon the medium. The primary radicals promote the breakdown of the peroxide in a chain reaction. The overall velocity of decomposition and composition of the products are governed by the nature of the solvent and the additives. S. R. Rafikov and V. S. Kudinova suggested that in the case of a solvent capable of attacking the peroxy group (ethyl alcohol), an exchange reaction occurs at a temperature below that of the breakdown of peroxide [3]. The main reaction is dehydrogenation of the alcohol:



The chain reaction here plays a secondary part.

The differences in behavior of acetyl peroxide and benzoyl peroxide are clearly manifested in reactions with acetic acid. Acetyl peroxide decomposes in glacial acetic acid to give a high yield of succinic acid, methane, CO_2 and methyl acetate. The mechanism of the reaction has been established by the work of Fry, Tolbert and Calvin [4]. Succinic acid was not detected among the reaction products when benzoyl peroxide was decomposed in boiling glacial acetic acid [5]. Galdstone [6] isolated benzene, diphenyl, CO_2 and benzoic, p-phenylbenzoic, homophthalic and homoterephthalic acids.

It appeared to us of interest to investigate the reactions of mixed acetyl benzoyl peroxide, which by dissociation of the O-O bond gives two radicals: $CH_3CO_2^{\cdot}$ and $C_6H_5CO_2^{\cdot}$. This enabled a comparison of their properties and provided new facts of interest in connection with the mechanism of reactions of acyl peroxides. Acetyl benzoyl peroxide was decomposed in methyl, isopropyl, n-butyl and tert-amyl alcohols and in glacial acetic acid.

Reaction of acetyl benzoyl peroxide with methyl, isopropyl and n-butyl alcohols gave CO_2, CH_4, benzoic and acetic acids and carbonyl compounds (see Table).

Judging by the amount of benzoic acid isolated and by the absence of benzene from the reaction products, the $C_6H_5COO^{\cdot}$ radical, without decomposing, removed hydrogen from the alcohol. Consequently, the CO_2 was released exclusively at the expense of the acetyloxy radical. Decarboxylation of the benxoyloxy radicals occurs when benzoyl peroxide reacts with alcohols. The absence of methyl benzoate and the equality in the volumes of CO_2 and CH_4 in the reactions investigated point to insignificant induced decomposition of acetyl benzoyl peroxide. Among the reaction products we found no diphenyl, benzene or esters of the solvent. The $CO_2 : CH_3COOH$ ratio depends upon the alcohol taken and the temperature. For methyl alcohol at 40° it is 2.3; at 64° it is 5.0; for isopropyl alcohol at 40° it is 0.8; at 82° it is 4.3; for tert-butyl alcohol it is 7.2; for n-butyl alcohol it is 9 at 90° and the molar peroxide/solvent ratio is 1:3.

Products isolated (in moles)	Solvents			
	CH_3OH*	$CH_3CHOHCH_3$**	n-C_4H_9OH***	CH_3COOH****
CO_2	0.0125	0.0193	0.0236	0.0344
CH_4	0.0125	0.02	0.023	0.0268
CH_3COOH	0.0025	0.0040	0.0039	—
C_6H_5COOH	0.0163	0.0282	0.0251	0.0024
CH_2O	0.0073	—	—	—
CH_3COCH_3	—	0.0286	—	—
n-C_3H_7CHO	—	—	0.0170	—
$C_6H_5COOCH_3$	—	—	—	0.0026
$HOOC(CH_2)_2COOH$	—	—	—	0.0178

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*0.0175 mole acetyl benzoyl peroxide in 80 ml alcohol was decomposed at 64°.

**0.0288 mole peroxide in 50 ml alcohol was decomposed at 82°.

***0.026 mole peroxide in 75 ml alcohol was decomposed at 90-95°.

****0.0299 mole peroxide in 75 ml glacial acetic acid was decomposed at 90°.

With the objective of clarifying the mechanism of reactions of the peroxide with alcohols, experiments were run at various reaction temperatures and with various concentrations of peroxide in different alcohols.

The velocity of decomposition of acetyl benzoyl peroxide by alcohols increased in the following order: tert-amyl < methyl < ethyl < isopropyl (Figs. 1-8), in agreement with the literature data cited above. The rate of evolution of gas and of decomposition of the peroxide increased linearly with the concentration.

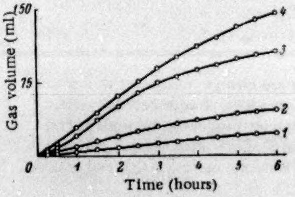

Fig. 1. Decomposition of the peroxide in CH_3OH at 50° (judged by volume of gas evolved). Peroxide/solvent ratio: 1) 1:150, 2) 1:75, 3) 1:30, 4) 1:15.

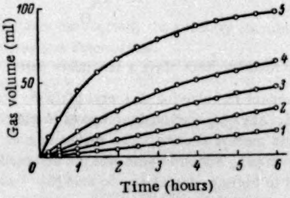

Fig. 2. Decomposition of 0.00333 mole peroxide in CH_3OH (1:75) (judging by volume of gas evolved). 1) 40°, 2) 45°, 3) 50°, 4) 55°, 5) 61°.

The data indicate that the reaction goes in two directions:

$$CH_3COOOCOC_6H_5 + RR'CHOH \begin{cases} \rightarrow C_6H_5COOH + CH_3COOH + RR'CO & \text{(a)} \\ \rightarrow C_6H_5COOH + CH_4 + CO_2 + RR'CO & \text{(b)} \end{cases}$$

At low temperatures the small evolution of gas in comparison with the degree of decomposition of peroxide indicated predominance of course (a). Two reaction routes are possible: intramolecular interaction and a free-radical mechanism. The presence of free acyloxy radicals in the solution was proved by reaction of the peroxide with alcohols in presence of diphenylpicrylhydrazine which had earlier been used for the suppression of induced decomposition of a peroxide [7]. In exploratory experiments with additions of diphenylpicrylhydrazine in the proportion of 0.5 mole per mole of peroxide hardly any gas was evolved under similar conditions; this indicated the absence of reaction (b) which went by a free-radical mechanism. Gas evolution commenced after disappearance of the color of the free diphenylpicrylhydrazine radical.

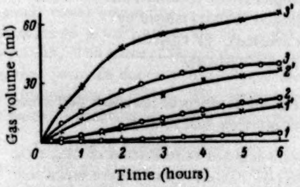

Fig. 3. Decomposition of 0.00166 mole peroxide in CH_3OH (1 : 150). Volume of gas evolved at temperatures of: 1) 40°; 2) 50°; 3) 61°; judged by decomposition of peroxide at temperatures of 1') 40°; 2') 50°; 3') 61°.

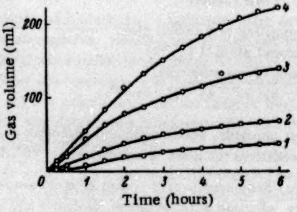

Fig. 4. Decomposition of peroxide in C_2H_5OH at 50° (judged by volume of gas evolved). Peroxide/solvent ratio: 1) 1:150, 2) 1:75, 3) 1:30, 4) 1:15.

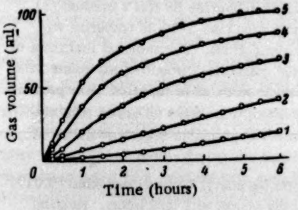

Fig. 5. Decomposition of 0.00333 mole peroxide in C_2H_5OH (1 : 75) (judged by the volume of gas evolved). 1) 40°, 2) 45° 3) 50°, 4) 55°, 5) 61°.

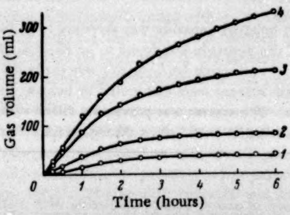

Fig. 6. Decomp. of peroxide in isopropyl alcohol at 50° (judged by volume of gas evolved). Peroxide/solvent ratio: 1) 1:150, 2) 1:75, 3) 1:30, 4) 1:15.

During the reactions we attempted to titrate the acid formed in course of reaction. This would have permitted an additional check on the rate of interaction of peroxide with alcohol. During titration of the original peroxide, however, we established that the alcoholic solution of peroxide reacts according to the following scheme in presence of 0.1 N caustic alkali:

$$2CH_3COOOCOC_6H_5 + NaOH \rightarrow (C_6H_5COO)_2 + CH_3COONa + CH_3COOOH.$$

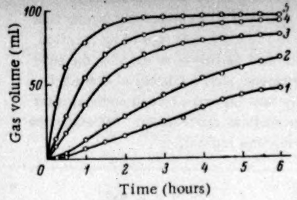

Fig. 7. Decomposition of 0.00333 mole peroxide in isopropyl alcohol (1 : 75) (judged by amount of gas evolved). 1) 40°, 2) 45°, 3) 50°, 4) 55°, 5) 61°.

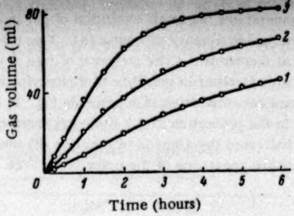

Fig. 8. Decomposition of 0.00333 mole peroxide in alcohols (1 : 75) (judged by volume of gas evolved). 1) CH_3OH, 2) C_2H_5OH, 3) iso-C_3H_7OH.

Benzoyl peroxide, acetic acid and peracetic acid were found among the products of reactions performed under various conditions (at room temperature, at −6°, in an atmosphere of nitrogen, and in air).

Thermal decomposition of acetyl benzoyl peroxide in glacial acetic acid led to formation of CH_4, CO_2, methyl benzoate, succinic acid, benzene, diphenyl and homophthalic acids (see Table). Quantitative separation of the reaction products presented great difficulties, so that our data do not give a full quantitative picture of the reaction. The products of reaction are the same as those given above for the decomposition of acetyl peroxide and benzoyl peroxide in acetic acid. In the present case decarboxylation of both RCOO– radicals is observed, as well as the formation of methyl benzoate, the latter fact indicating the possibility of initiated decomposition:

$$CH_3\cdot + CH_3COOOCOC_6H_5 \longrightarrow C_6H_5COOCH_3 + CH_3COO\cdot$$

EXPERIMENTAL

Acetyl benzoyl peroxide was prepared from benzaldehyde and acetic anhydride by Nef's method [8]. The activity of the peroxide was found to be 93-98% by iodometric determination (the 2-7% of impurity was benzoic acid). A correction for impurity was made during the acidity determinations. The thermal reactions of the peroxide with solvent were conducted by heating in a flask with a reflux condenser (ground-glass connection) on a water bath. The system was previously filled with nitrogen. The gaseous products of reaction were passed through traps cooled to −15°, then through traps containing 40% KOH for absorption of the CO_2; the residual CH_4 was collected in a buret. The methane was determined by combustion in a VTI (All-Union Heat Engineering Institute) apparatus.

Reaction of acetyl benzoyl peroxide with methyl alcohol. 3.3 g 95.5% acetyl benzoyl peroxide (0.0175 mole) in 50 ml CH_3OH was added portionwise to 30 ml methyl alcohol in the course of 1 1/2 hours. Heating at the boiling point of the solvent was usually continued for 3.5-4 hours. After this period 0.55 g (0.0125 mole) CO_2 and 0.0125 mole methane had come off. The methanol solution was titrated with 0.1 N KOH. The total acidity of the solution was 0.0188 mole. Acidification yielded 1.99 g benzoic acid (0.0163 mole) with m. p. 121° (from water). The presence of acetic acid was confirmed by the cacodyl oxide test. Its amount was determined by difference on the basis of the total acidity and the C_6H_5COOH isolated; it was 0.0025 mole. 2.14 g of the dimedon derivative of formaldehyde with m. p. 188° (from alcohol) was isolated. Esters were not detected.

Reaction of acetyl benzoyl peroxide with isopryopyl alcohol. The reaction was conducted by the above procedure. 5.4 g 96% acetyl benzoyl peroxide (0.0288 mole) in 50 ml isopropyl alcohol was heated for 3 hours at the boiling point of the solvent. During the reaction 0.85 g CO_2 (0.0193 mole) and 448 ml (0.02 mole) methane were evolved. The total acidity was 0.0322 mole. Acidification yielded 3.7 g benzoic acid (0.0282 mole). The difference between the total acidity and the amount of C_6H_5COOH gave a yield of 0.004 mole acetic acid, the presence of which was confirmed by qualitative reactions. 1.55 g of acetone 2,4-dinitrophenylhydrazone (0.0269 mole) was isolated; m. p. (from alcohol) 126°. 0.0286 mole acetone was found by titration of the oxime. No esters were found.

Reaction of acetyl benzoyl peroxide with n-butyl alcohol. 5.0 g 93.5% acetyl benzoyl peroxide (0.026 mole) in 75 ml n-butyl alcohol was heated at 90-95° for 4 hours, giving 1.03 g CO_2 (0.0236 mole) and 542 ml (0.023 mole) methane. Total acidity 0.0290 mole. 3.37 g (0.0251 mole) benzoic acid was separated. The acetic acid content was estimated as 0.0039 mole. n-Butyraldehyde was detected in the first fraction of the distillate. Semicarbazone, m. p. 103°. Dimedon derivative, m. p. 133°. Determination by titration of the oxime [9] gave 0.017 mole n-butyraldehyde. No esters were found.

Reaction of acetyl benzoyl peroxide with dimethylethyl carbinol. Heating of 3.2 g 94% acetyl benzoyl peroxide (0.0166 mole) in 60 ml dimethylethyl carbinol for 20 hours at 50° did not lead to appreciable evolution of gases. Esters, acids and olefins were found in the reaction products after reaction at 80-90°.

Some kinetic data for reactions of acetyl benzoyl peroxide with alcohols.* Reactions were performed in a small vessel with a fused-on reflux condenser in a nitrogen atmosphere. Heating was carried out in a thermostat (accurate to ± 0.1°) at 40, 45, 50, 55 and 61°. The peroxide/alcohol molar ratios were: 1:150, 1:75, 1:30, and 1:15. The gases (CO_2 + CH_4) were collected in a gas buret over mercury, and from their quantity the percentage peroxide decomposing in accordance with equation (b) was calculated. Carbon dioxide was determined gravimetrically as $BaCO_3$. The peroxide content after heating was determined iodometrically, and the percentage of peroxide reacting according to equations (a) and (b) was calculated (Figs. 1-8).

Reaction of acetyl benzoyl peroxide with glacial acetic acid. 6.0 g 94.5% acetyl benzoyl peroxide (0.0316 mole) in 30 ml glacial acetic acid was added in portions in the course of half an hour to 45 ml glacial acetic acid heated to 90°. Heating was continued for 1 1/2 to 2 hours. After this period, 95% of the peroxide (0.0299 mole) had reacted to give 1.52 g CO_2 (0.0344 mole) and 600 ml methane (0.0268 mole). The first fraction of solvent distillate was nitrated and gave 0.63 g m-dinitrobenzene with m. p. 90° (from alcohol), equivalent to 0.0040 mole benzene. The main bulk of the acetic acid came over at 44-45° (45 mm). The residue was kept in a vacuum-desiccator until it started to crystallize, and then washed with sodium carbonate. The insoluble portion was extracted with ether. The ether was driven off and the 0.35 g of residue was saponified with alcoholic alkali. Analysis revealed the presence of 0.0026 mole ester. The neutralized solution was steam-distilled. A small amount of diphenyl was detected; m. p. 69° (a mixture with authentic diphenyl melted at 70°). In the residue after steam distillation was found 0.3 g benzoic acid (0.0024 mole) with m. p. 121° (from water). Acidification of the concentrated sodium carbonate solution gave 2.1 g succinic acid (0.0178 mole) with m. p. 183°. No depression of melting point occurred in a mixed test with pure, authentic succinic acid. The identity of the acid was confirmed by the pyrrole reaction. From the mother liquor, following separation of the succinic acid, was isolated 1.03 g of white acid, probably a mixture of homophthalic acids. In the oxidation of this solid the formation of o-phthalic acid was established by the resorcinol reaction.

Reaction of acetyl benzoyl peroxide with caustic alkali. 0.3910 g 96.8% acetyl benzoyl peroxide (0.00217 mole) in 20 ml isopropyl alcohol was titrated with 0.1 N KOH in presence of phenolphthalein at −6°. The total acidity was 0.00117 mole; during the treatment, 0.22 g (0.00091 mole) benzoyl peroxide separated; m. p. 106°. The melting point of a mixture with pure benzoyl peroxide was 106.5°. The benzoyl peroxide was determined iodometrically. The filtrate after separation of the benzoyl peroxide was acidified and the acetyl hydroperoxide content determined iodometrically; the amount was 0.00111 mole.

The authors thank V. A. Shushunov for assisting in the evaluation of the results.

SUMMARY

1. Reactions of acetyl benzoyl peroxide with methyl, ethyl, isopropyl and n-butyl alcohols were investigated.

2. The reactions go with dehydrogenation of the alcohol and formation of a mixture of acetic and benzoic acids on the one hand, or with formation of benzoic acid, methane and CO_2 on the other hand.

3. The velocity of reaction with the alcohols decreases in the order: isopropyl > ethyl > methyl> tert-amyl.

4. Addition of diphenylpicrylhydrazine inhibits the reaction that goes with evolution of gas.

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* B. Redoshkin collaborated in these experiments.

5. Reaction of acetyl benzoyl peroxide in acetic acid gave methane, CO_2, methyl benzoate, succinic acid, benzene, diphenyl and homophthalic acids.

6. Treatment of the alcoholic solution of the peroxide with caustic alkali results in formation of benzoyl peroxide, acetic acid and peracetic acid.

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Gorky State University

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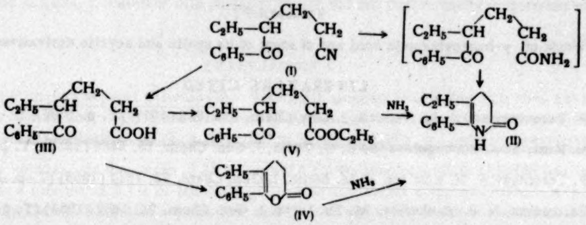
SYNTHESES WITH THE HELP OF ACRYLONITRILE

XXVIII. γ-BENZOYLCAPROIC ACID AND ITS DERIVATIVES

A. N. Kost and A. P. Terentyev

δ-Ketonitriles, obtained by cyanoethylation of ketones, can serve as starting substances for synthesis of a series of heterocyclic systems, namely, piperidines [1], α-piperidones [2], pyrrolines [3] and lactones [4].

We previously described the hydrolysis of δ-ketonitriles to the corresponding amides [3]. In the case of γ-benzoylcapronitrile (I), which is formed by the action of acrylonitrile on butyrophenone, we failed to obtain the amide. Hydrolysis with hydrogen peroxide gave an oil which did not crystallize after standing for a year and which changed into the unsaturated lactam (II) during vacuum distillation. Hydrolysis of nitrile (I) with hydrochloric acid gave γ-benzoylcapronitrile (III), which on distillation with hydrochloric acid and magnesium sulfate was transformed into the unsaturated lactone (IV). This lactone, just like the ethyl ester of γ-benzoylcaproic acid (V), gives the same lactone (II) on ammonolysis.



EXPERIMENTAL

γ-Benzoylcapronitrile (I). 10.6 g acrylonitrile was added dropwise in the course of 1/2 hour to a mixture of 50 g butyrophenone and sodium ethoxide (0.2 g sodium in 5 ml alcohol) with stirring. Stirring was then continued for an hour at room temperature; the mixture was left overnight, carefully neutralized with glacial acetic acid and distilled in vacuum. Original butyrophenone (b. p. 85-90° at 4 mm) came over first, followed by 25 g (62%) of nitrile (I) with b. p. 155-160° (5 mm). After a second distillation the substance had the constants:

B. p. 153-154° (4 mm), n_D^{20} 1.5232, d_4^{20} 1.0420. MR_D 59.02; calc. 58.74.
Found %: N 7.16, 7.37. $C_{13}H_{15}ON$. Calculated %: N 6.96.

γ-Benzoylcaproic acid (III). A mixture of 8.0 g nitrile (I) and 100 ml concentrated hydrochloric acid was boiled 40 hours. It was then diluted to double the volume with water and extracted with ether; the extract was washed with aqueous alkali and the alkali extract was strongly acidified and again extracted with ether. After removal of the ether, the residue was distilled in vacuum to give 8.0 g (92%) acid (III):

B. p. 214° (7 mm), n_D^{20} 1.5270, d_4^{20} 1.1183, MR_D 60.55; Calc. 60.18.
Found %: C 70.90, 71.07; H 7.42, 7.59. $C_{13}H_{16}O_3$. Calculated %: C 70.88; H 7.32.

Ethyl ester of γ-benzoylcaproic acid (V). 5.5 g acid (III), 7 ml anhydrous ethyl alcohol and 0.05 g p-toluenesulfonic acid were boiled 12 hours. 5 ml toluene was then added, the water, alcohol and toluene were distilled off at 68-70°, another 7 ml alcohol was added, and the operation was repeated. After extraction with alcohol, washing with saturated sodium carbonate solution, drying with sodium sulfate and distilling, 3.24 g (52%) of ester (V) was obtained:

B. p. 170-171° (8 mm), n_D^{20} 1.5052, d_4^{20} 1.0512, MR_D 70.06; Calc. 69.63.
Found %: C 72.27, 72.49; H 8.08, 8.17. $C_{15}H_{20}O_3$. Calculated %: C 72.55; H 8.12.

3-Ethyl-2-phenyl-4,5-dihydropyrone-6 (IV). To a solution of 10 g of acid (III) in 50 ml ether was added 3 ml concentrated hydrochloric acid and 1 g anhydrous magnesium sulfate. The mixture was boiled 1 hour, the ether was driven off, and the residue was distilled in vacuum. Yield 6.1 g (67%) unsaturated δ-lactone (IV):

B. p. 183-185° (20 mm), n_D^{20} 1.5440, d_4^{20} 1.1117, MR_D 57.43; Calc. 57.62.
Found %: C 77.29, 77.37; H 6.98, 7.03. $C_{13}H_{14}O_2$. Calculated %: C 77.20; H 6.98.

3-Ethyl-3-phenyl-4,5-dihydropyridone-6 (II). Shaking of lactone (IV) with a fivefold molar amount of 30% aqueous ammonia gave the unsaturated lactam (II) in 79% yield, m. p. 110-110.5° (from ether).

Found %: C 77.34, 77.54; H 7.48, 7.57. $C_{13}H_{15}ON$. Calculated %: C 77.58; H 7.51.

The same substance was similarly prepared (yield 62%) from ester (V). Saponification of nitrile (I) with alkaline hydrogen peroxide by the previsously described procedure [3] gave a non-crystallizing oil from which by vacuum distillation was obtained a small amount of acid (III) and a 50% yield of the unsaturated lactam (II), b. p. 174° (3mm), m. p. 110° (from ether). The latter does not give a depression of melting point in admixture with the product of ammonolysis of the lactone(II) or ester (V).

SUMMARY

The synthesis of γ-benzoylcaproic acid and of some of its cyclic and acyclic derivatives is described.

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Moscow State University

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SYNTHESIS OF SOME HALO DERIVATIVES OF BENZOPHENONE

B. V. Tronov and E. S. Novikova

The method of iodination of aromatic compounds in presence of nitric-sulfuric nitrating mixture, developed in our laboratory [1], has made m-iodobenzoic acid a readily accessible substance. It appeared of interest to prepare a series of previously unknown derivatives of this acid.

In the present paper we describe the synthesis of some ketones by the Friedel-Crafts method from m-iodobenzoyl chloride and various aromatic compounds (Table 1). Comparison of the quantitative results of the syntheses showed that hydrocarbons (naphthalene, toluene, benzene) react the most easily with the acid chloride, monohalo derivatives of benzene react with more difficulty, and dihalo derivatives react with still greater difficulty; p-diiodobenzene gave a higher yield of ketone than dibromobenzene, while dichlorobenzene did not react at all. The structure of the ketones was determined by alkaline cleavage. Ketones prepared from monohalobenzenes cleaved to iodobenzene and the p-halo-substututed benzoic acid, i. e. the synthesis had gone with substitution of the hydrogen in the para position to the halogen. It was also significant that m-iodophenol was more easily detached from the carbonyl carbon than p-iodophenol. Oximes and semicarbazones were prepared from the majority of the ketones. Treatment with phenylhydrazine did not lead to easily separatable crystalline products.

EXPERIMENTAL

Preparation of m-iodobenzoyl chloride [2]. Equimolar amounts of acid and PCl_5 were heated at 130-135° on an oil bath for half an hour. $POCl_3$ was driven off by distillation on a water bath under reduced pressure, and then the acid chloride was distilled off (b. p. 159-160° at 23 mm; liquid at the ordinary temperature).

Synthesis of ketones. In the course of 30 minutes 3.6 g anhydrous aluminum chloride was introduced in small portions into a mixture of 6.7 g m-iodobenzoyl chloride and excess of the other reactant (e. g. 5.9 g benzene). The mixture was heated on a water bath at 50°. The end of the reaction was indicated by cessation of evolution of hydrogen chloride. The ketone was separated by pouring the reaction mixture into 200 ml ethyl alcohol cooled with ice and salt. The precipitate was recrystallized from alcohol.

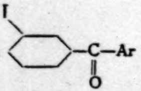
The ketones are colorless, crystalline substances, soluble in benzene, ether, and hot alcohol. Results of analyses are presented in Table 2.

Determination of structure of the ketones. A weighed sample of ketone was heated with a mixture of NaOH and KOH at 250° for 3 hours; distillation gave iodobenzene. Thus, 3.08 g iodobenzophenone gave 0.8 g C_6H_5I with b. p. 189°, d_4^{20} 1.8, iodine content 60.2 %, calculated 60.8%. The cooled melt was leached out with water. Treatment of the aqueous solution with dilute sulfuric acid brought down the free aromatic acids which were purified by sublimation or crystallization. m-$IC_6H_4COC_6H_5$ gave benzoic acid; m-$IC_6H_4COC_6H_4Cl$ gave p-chlorobenzoic acid with m. p. 234-235°; found halogen 23.5%, M 155.1; calculated halogen 22.7%, M 156.5. m-$IC_6H_4COC_6H_4I$ gave p-iodobenzoic acid with m. p. 270°; found iodine 51%, M 248.4; calculated iodine 51.1%, M 247.9.

Oximes and semicarbazones of the ketones were prepared by heating the ketones with hydroxylamine hydrochloride and semicarbazide hydrochloride and sodium acetate in alcoholic solution. They were purified by crystallization from alcohol. Melting points are listed in Table 1 and analyses in Table 3.

TABLE 1

Ketones



Ketone No.	Name	Ar in formula	Reactants condensed with m-IC_6H_4COCl		Yield of ketones (%) after the following hours of heating				Melting point		
			formula	amount reacted with 6.7 g m-IC_6H_4COCl	6	12	24	48	of ketones	of oximes	of semicarbazones
1	m-Iodobenzophenone	C_6H_5	C_6H_6	5.9 g	71	52	61	62	44°	185—186°	160—162°
2	m-Iodophenyl-p'-tolyl ketone	p-$CH_3C_6H_4$	$C_6H_5CH_3$	2.3	70	81.2	81.3	81	114	183—184	171—172
3	m-Iodophenyl-α-maphthylketone	α-$C_{10}H_7$	$C_{10}H_8$	3.2	50	91	91	91.5	93—94	—	—
4	m-Iodo-p'-fluorobenzophenone	p-C_6H_4F	C_6H_5F	4.8	24	38	50	51	84—85	131—132	178—179
5	m-Iodo-p'-chlorobenzophenone	p-C_6H_4Cl	C_6H_5Cl	8.7	50	58	60	60.8	135	173—174	174—175
6	m-Iodo-p'-bromobenzophenone	p-C_6H_4Br	C_6H_5Br	11.9	23	37	50	53	155	179—180	208—209
7	m,p'-Diiodobenzophenone	p-C_6H_4I	C_6H_5I	5.8	16.6	33.3	40	41	173	179—180	210—211
8	m-Iodo-o',m'-dichlorobenzophenone	o,m-$C_6H_3Cl_2$	p-$C_6H_4Cl_2$	3.6	—	—	—	—	—	—	—
9	m-Iodo-o',m'-dibromobenzophenone	o,m-$C_6H_3Br_2$	p-$C_6H_4Br_2$	8.2	—	—	—	20	150	—	—
10	m,o',m'-Triiodobenzophenone	o,m-$C_6H_3I_2$	p-$C_6H_4I_2$	8.2	—	—	—	28	158—159	—	—

TABLE 2

Analysis of Ketones

Ketone No.	Formula	Found		Calculated	
		halogen (%)	*M*	halogen (%)	*M*
1	$C_{13}H_9OI$	41.88	304.1	41.20	308.0
2	$C_{14}H_{11}OI$	38.44	320.1	39.41	321.9
3	$C_{17}H_{11}OI$	36.00	353.6	35.40	358.9
4	$C_{13}H_8OFI$	5.49 (F) 38.80 (I)	322.1	5.82 (F) 38.51 (I)	325.9
5	$C_{13}H_8OClI$	46.50	344.0	47.40	342.5
6	$C_{13}H_8OBrI$	53.40	387.0	53.90	386.9
7	$C_{13}H_8OI_2$	56.50	433.9	57.10	433.8
9	$C_{13}H_7OBr_2I$	61.44	466.0	61.65	465.7
10	$C_{13}H_7OI_3$	67.61	556.9	68.01	559.7

TABLE 3

Analysis of Derivatives of Ketones

Ketone No.	Derivative	Formula	Found (%)		Calculated (%)	
			halogen	nitrogen	halogen	nitrogen
1	Oxime	$C_{13}H_9ONI$	39.1	4.2	39.42	4.34
	Semicarbazone	$C_{14}H_{12}ON_3I$	33.99	11.3	34.46	11.56
2	Oxime	$C_{14}H_{12}ONI$	37.10	3.85	37.66	4.15
	Semicarbazone	$C_{15}H_{14}ON_3I$	33.12	10.92	33.49	11.09
4	Oxime	$C_{13}H_9ONFI$	5.30	3.99	5.57	4.10
	Semicarbazone	$C_{14}H_{11}ON_3FI$	4.85	10.57	4.9 (F)	10.88
5	Oxime	$C_{13}H_9ONClI$	45.30	3.75	45.41	3.91
	Semicarbazone	$C_{14}H_{11}ON_3ClI$	40.69	10.57	40.66	10.51
6	Oxime	$C_{13}H_9ONBrI$	51.5	3.47	51.34	3.36
	Semicarbazone	$C_{14}H_{11}ON_3BrI$	46.77	9.17	46.66	9.46
7	Oxime	$C_{13}H_9ONI_2$	56.76	3.36	56.55	3.47
	Semicarbazone	$C_{14}H_{11}ON_3I_2$	51.76	8.26	51.71	8.55

SUMMARY

A study was made of the reaction of m-iodobenzoyl chloride with some aromatic hydrocarbons and halo derivatives in presence of aluminum chloride.

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Tomsk Polytechnic Institute

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THE SULFONATION OF 2-CHLORONAPHTHALENE

I. SULFONATION AT LOW TEMPERATURE

N. N. Vorozhtsov, Jr., and N. N. Karandasheva

Sulfonation of 2-chloronaphthalene was performed by Arnell and by Armstrong and Wynne with oleum at 130-140° [1] and with chlorosulfonic acid in the cold [2, 3]; the products were identified as 2-chloronaphthalene-8-sulfonic acid and 2-chloronaphthalene-6-sulfonic acid; the amount of the latter increases with rising temperature and duration of sulfonation. Sulfonation of 2-bromonaphthalene with chlorosulfonic acid similarly gave 2-bromonaphthalene-8-sulfonic acid and 2-bromonaphthalene-6-sulfonic acid [2, 4, 5]. Sulfonation of 2-iodonaphthalene under the same conditions led to 2-iodonaphthalene-8- and-5-sulfonic acids [2, 5, 6], but heating of the products of sulfonation for 5 hours at 150° converted both acids into 2-iodonaphthalene-6-sulfonic acid. Armstrong and Wynne, in the light of these results, suggested the possibility of formation of the 5-sulfonic acid during sulfonation of all the three 2-halonaphthalenes. In their opinion, however, 2-bromo- and 2-chloronaphthalene-5-sulfonic acids are unstable and rearrange even in the cold to the 6-sulfonic acids, whereas rearrangement of 2-iodonaphthalene-5-sulfonic acid occurs only at 150° [6]. The papers cited do not give a complete picture of the sulfonation of 2-chloronaphthalene. The sulfonation with monohydrate and with oleum at low temperature, a matter of practical interest, remained uninvestigated. Furhter work was also needed on the authors's method of fractionation of the mixture of products of sulfonation. Their method was based on the differing solubilities of the lead or potassium salts of the sulfonic acids without subsequent fractional crystallization of the chlorides prepared from them.

We treated 2-chloronaphthalene with monohydrate at 20° and obtained 2-chloronaphthalene-8-sulfonic acid (approx. 70%) and 2-chloronaphthalene-5-sulfonic acid (approx. 30%) (Experiment 1). Contrary to the opinion of Armstrong and Wynne, 2-chloronaphthalene-5-sulfonic acid was relatively stable under the conditions of sulfonation. Thus, the content of 5-sulfonic acid in the above mixture hardly changed when heated for 5 hours at 70-75°, although the content of the 8-sulfonic acid changed appreciably due to concomitant processes of sulfonation to 2-chloronaphthalene-6,8-disulfonic acid and isomerization to 2-chloronaphthalene-6-sulfonic acid (Experiments 2 and 3). The action of oleum on the same sulfonic acid mass lowered the content of the 5-sulfonic acid to 16%. while the 8-sulfonic acid disappeared completely. Increase in the duration of sulfonation with monohydrate to 1460 hours led to complete disappearance of the 5-sulfonic acid (Experiment 5).

When the anhydrous potassium salt of 2-chloronaphthalene-5-sulfonic acid was introduced into monohydrate, no appreciable isomerization occurred after 24 hours at 20° or 3 hours at 50° (Experiment 6). After 22 hours in weak oleum at 20°, the 5-sulfonic acid was sulfonated to 2-chloronaphthalene-5,7-disulfonic acid, although here again no appreciable isomerization took place (Experiment 7).

We failed to isolate 2-chloronaphthalene-1-sulfonic acid from the mixture of reaction products. In order to establish whether the failure of this attempt to isolate the acid was due to its instability, we investigated the reaction of the anhydrous potassium salt of 2-chloronaphthalene-1-sulfonic acid with monohydrate for 20 hours at 20°. This reaction gave a considerable amount of 2-chloronaphthalene-1,5-disulfonic acid and a small amount of 2-chloronaphthalene-8-sulfonic acid; about half of the 2-chloronaphthalene-1-sulfonic acid taken in the reaction was unchanged (Experiment 8). It can be assumed that 2-chloronaphthalene-1-sulfonic acid is generally not formed when 2-chloronaphthalene is sulfonated with monohydrate at room temperature; if the contrary was the case, it should have been possible to detect either the sufficiently stable 1-sulfonic acid or the product of its sulfonation – 2-chloronaphthalene-1,5-disulfonic acid.

EXPERIMENTAL

The 2-chloronaphthalene used for the experiments was obtained by isomerization of 1-chloronaphthalene [7] and was distilled and recrystallized several times from methanol; solidification point 56.9°, m. p. 57.7-58.0°. Sulfonation was conducted in a three-necked flask with stirring. At the conclusion of sulfonation, the sulfonated mass was poured into a mixture of water and ice and neutralized with calcium carbonate. Potassium carbonate was added to the filtrate from the gypsum and the solution of potassium salts, after filtration from calcium carbonate, was fractionally crystallized by evaporation. The fractions of potassium salts obtained in this fashion were mixtures of salts of the sulfonic acids. Simple recrystallization of the potassium salts generally failed to completely separate the sulfonic acids. The best separation of the mixture of sulfonation products was achieved by fractional crystallization of the potassium salts of the sulfonic acids into 2-4 fractions followed by fractional crystallization of the chlorides prepared from them. The potassium salts of the sulfonic acids were converted into chlorides by treatment with phosphorus pentachloride at 100-110° in the case of monosulfonic acids and at 120-130° in the case of disulfonic acids. The crude sulfochloride was recrystallized several times from glacial acetic acid (7-10 ml solvent for 1 g chloride). The mother liquor, containing the more soluble chloride, was diluted with water (1 : 1) and the resultant precipitate recrystallized from dilute acetic acid (1 : 1). If the crude chloride consisted of a low-melting mixture which could not be recrystallized from acetic acid and other solvents (benzene, dichloroethane), then the mixture of chlorides was converted into a mixture of anilides or amides; the latter in turn were subjected to fractional crystallization (from alcohol, benzene, dichloroethane, carbon tetrachloride). Amides and anilides were prepared from the chlorides by the normal method. Their identity was confirmed by determination of the mixed melting points of each of the prepared crystalline chlorides, amides and anilides with chlorides, amides and anilides of sulfonic acids of 2-chloronaphthalene of known structure, synthesized from the corresponding sulfonic acids of 2-naphthylamine via the diazo compounds. Below we describe the derivatives of the sulfonic acids of 2-chloronaphthalene that were obtained in this fashion.

2-Chloronaphthalene-1-sulfonic acid. The benzylthiuronium salt – rectangular plates (from methyl alcohol), m. p. 188.2° (all melting points were determined with a calibrated shortened thermometer).

Found %: N 7.06. $C_{18}H_{17}O_3N_2S_2Cl$. Calculated %: N 6.85.

Aniline salt – long plates from water, m. p. above 250° (with decomp.).

Found %: N 4.10. $C_{16}H_{14}O_3NSCl$. Calculated %: N 4.17.

Chlorides – plates from glacial acetic acid, m. p. 76°; the literature gives m. p. 74-75° [8]. Amide – needles from aqueous alcohol, m. p. 153.8°; the literature gives m. p. 153° [9]. Anilide – tapered needles from alcohol, m. p. 137.2°.

Found %: N 4.57. $C_{16}H_{12}O_2NSCl$. Calculated %: N 4.40.

2-Chloronaphthalene-5-sulfonic acid. Chloride – needles from glacial acetic acid, m. p. 70°; the literature also gives 70° [10, 11]. Amide – needles from aqueous alcohol, m. p. 212.5° (with decomp.); the literature gives 214° [9-11]. Anilide – long plates from aqueous alcohol, m. p. 172.5°.

Found %: N 4.55. $C_{16}H_{12}O_2NSCl$. Calculated %: N 4.40.

2-Chloronaphthalene-6-sulfonic acid. Benzylthiuronium salt – needles from methyl alcohol, m. p. 194.2°.

Found %: N 6.993. $C_{18}H_{17}O_3N_2S_2Cl$. Calculated %: N 6.85.

Chloride – prisms from glacial acetic acid, m. p. 110°; the literature gives 109° [8] and 110° [12]. Amide – needles from aqueous alcohol, m. p. 185.6°; the literature gives 184° [9, 12]. Anilide – needles from aqueous alcohol, m. p. 121.5°.

Found %: N 4.47. $C_{16}H_{12}O_2NSCl$. Calculated %: N 4.40.

2-Chloronaphthalene-7-sulfonic acid. Chloride – tablets from dilute acetic acid, m. p. 86°; the literature gives 86.5° [10, 13], 84.5-85° [8]. Amide – needles from aqueous alcohol, m. p. 178°; the literature gives 176° [9, 10, 13]. Anilide – rectangular plates from aqueous alcohol, m. p. 147.4°.

Found %: N 4.32. $C_{16}H_{12}O_2NSCl$. Calculated %: N 4.40.

2-Chloronaphthalene-8-sulfonic acid. Benzylthiuronium salt – radially grouped needles from aqueous alcohol, m. p. 146.5°.

Found %: N 6.96. $C_{18}H_{17}O_3N_2S_2Cl$. Calculated N 6.85.

Aniline salt – long plates from water, m. p. 248-249°.

Found %: N 4.31. $C_{16}H_{14}O_3NSCl$. Calculated %: N 4.17.

Chloride – needles from glacial acetic acid, m. p. 132°; 127° [8, 11, 12], 124-126° [14]. Amide-needles from aqueous alcohol, m. p. 237°; the literature gives 235° [8, 9, 11, 12], 231-232° [14]. Anilide – long plates from aqueous alcohol, m. p. 157°.

Found %: N 4.54. $C_{16}H_{12}O_2NSCl$. Calculated %: N 4.40.

2-Chloronaphthalene-1,5-disulfonic acid. Dichloride – long plates from glacial acetic acid, m. p. 160°; the literature gives m. p. 158° [15]. Dianilide-needles from alcohol, m. p. 239°.

Found %: N 5.80. $C_{22}H_{17}O_4N_2S_2Cl$. Calculated %: N 5.92.

2-Chloronaphthalene-5,7-disulfonic acid. Dichloride – needles from glacial acetic acid, m. p. 157°; the literature gives m. p. 156° [11, 15]. Diamide – needles from alcohol, m. p. above 300°.

Found %: N 8.81. $C_{10}H_9O_4N_2S_2Cl$. Calculated %: N 8.74.

Dianilide – long plates from aqueous alcohol, m. p. 207.5°; the literature gives m. p. 206° [9].

2-Chloronaphthalene-6,8-disulfonic acid. Dichloride – needles from glacial acetic acid, m. p. 173°; literature m. p. 170° [11, 15]. Diamide – long plates from aqueous alcohol, m. p. 269° (with decomp.); the literature gives 250° [15]. Dianilide – rhombic plates from aqueous alcohol, m. p. 193°; the literature gives m. p. 192° [9].

Sulfonation of 2-chloronaphthalene with monohydrate at 20°. Experiment 1. To 35.3 g 100% monohydrate (0.36 mole) was added 9.8 g 2-chloronaphthalene (0.06 mole). Sulfonation at 20° was performed for 3 hours. Crystals began to come down in the sulfonic acid mass 2 hours after the start of the experiment. The sulfonic acid mass was worked up to give three fractions of potassium salts of sulfonic acids of 2-chloronaphthalene. The 1st fraction of potassium salts (5.10 g) was converted into 2.18 g of a mixture of chlorides; fractional crystallizations of the latter gave 0.75 chloride less soluble in glacial acetic acid, m. p. 132° (2-chloronaphthalene-8-sulfochloride). Dilution of the mother liquors with water brought down a more-soluble low-melting chloride which was transformed into the amide (0.60 g), with m. p. 207-208°; a mixed sample with authentic 2-chloronaphthalene-5-sulfamide had m. p. 210°. Of the 9.60 g of potassium salts of the 2nd fraction, 4.00 g was converted into 3.50 g of a mixture of chlorides; fractional crystallizations of the latter from glacial acetic acid gave 1.40 g chloride with m. p. 132°, and a low-melting, more soluble chloride which was converted into 0.40 g anilide. Fractional crystallization of the latter from alcohol and aqueous alcohol gave 3 fractions of anilide with m. p. 171-171.5°, 168-168.5° and 171.5-172°; the melting points of mixed samples of each fraction with authentic 2-chloronaphthalene 5-sulfanilide were 172, 170-170.5 and 172°. The 3rd fraction of potassium salts (4.50 g) was converted into 4.32 g of a mixture of chlorides from which after fractional crystallization was obtained 2.20 g of a chloride with m. p. 130.5-131.5° and a more soluble, low-melting chloride which was converted into 1.05 g amide with m. p. 212°; a mixture with 2-chloronaphthalene-5-sulfamide had m. p. 212°. Consequently, the main products of sulfonation are 2-chloronaphthalene-8-sulfonic acid (approx. 70%) and 2-chloronaphthalene-5-sulfonic acid (approx. 30%).

Experiment 2. The sulfonic acid mass obtained under the conditions of Experiment 1 (the charge of 2-chloronaphthalene was 0.03 mole) was stirred for 3 hours at 20° and then heated 1 hour at 70°. From the 1st fraction of potassium salts (6.7 g) was obtained 4.58 g of a mixture of chlorides of 2-chloronaphthalene-8-sulfonic acid and 2-chloronaphthalene-5-sulfonic acid in the ratio of 4 : 1; from the 2nd fraction of potassium salts (5.2 g) was obtained 2.86 g of a mixture of chlorides of the same acids in the ratio of 3 : 1. The main components of the mixture were 2-chloronaphthalene-8-sulfonic acid (approx. 78%) and 2-chloronaphthalene-5-sulfonic acid (approx. 22%).

Experiment 3. The sulfonated mass obtained under the conditions of Experiment 1 (amount of 2-chloronaphthalene 0.03 mole) was stirred 5 hours at 70-75°. Two fractions of potassium salts of sulfonic acids were obtained. The 1st fraction (3.24 g) was transformed into 3.08 g of a mixture of chlorides. Fractional crystallization of the chlorides less soluble in glacial acetic acid gave fractions (total weight 0.58 g) with m. p. 110-111, 106-107.5, and 111°; mixed samples with authentic 2-chloronaphthalene-6-sulfochloride had m. p. 110.5°, 108-108.7° and 110.5°. The low-melting mixture of chlorides with better solubility in glacial acetic acid was converted to the anilide, from which by fractional crystallization from alcohol and aqeuous alcohol were obtained fractions of anilide (total weight 0.22 g) with m. p. 156-156.3 and 156.5°; the melting point of mixed specimens with authentic 2-chloronaphthalene-8-sulfanilide was 157°. The low-boiling mixture of chlorides with the highest solubility in glacial acetic acid was converted to anilide whose melting point after recrystallization from alcohol and benzene was 169.5-170.5° (0.04 g); a mixture with 2-chloronaphthalene-5-sulfanilide had m. p. 171°. The 2nd fraction of potassium salts (7.09 g) was transformed into 4.29 g of a mixture of chlorides. The chloride (0.32 g) least soluble in glacial acetic acid had m. p. 169-170° (2-chloronaphthalene-6,8-disulfochloride, mixed melting point 171-171.5°). The low-melting chloride with better solubility in glacial acetic acid was converted to the anilide from which by fractional crystallization from benzene and alcohol were obtained two fractions of anilide (total weight 0.22 g) with m. p. 171-171.5 and 168-169°; mixtures with authentic anilide of 2-chloronaphthalene-5-sulfonic acid had m. p. 172 and 170-170.5°. Consequently, the mixture of sulfonation products contained 2-chloronaphthalene-5-sulfonic acid (approx. 23%), 2-chloronaphthalene-8-sulfonic acid (approx. 10%), 2-chloronaphthalene-6-sulfonic acid (approx. 30%) and 2-chloronaphthalene-6,8-disulfonic acid (approx. 37%).

Experiment 4. To the sulfonic acid mass prepared under the conditions of Experiment 1 (0.03 mole 2-chloronaphthalene) was added 4.8 g free SO_3 (0.06 mole) in the form of 21.4% oleum (11.6 ml); the initial concentration of the sulfonating agent during sulfonation was 6.4% SO_3. Stirring was continued for another 3 hours at 20°. The mass crystallized towards the end of the operation. Two fractions of potassium salts of 2-chloronaphthalene-5-sulfonic acid were obtained (0.67 and 0.76 g); these were converted via the chloride into the amide with m. p. 214°. In addition three fractions of potassium salts of 2-chloronaphthalene-6,8-disulfonic acid were obtained (2.13, 3.23 and 0.72 g); their dichlorides had m. p. 172-172.5, 172.3-172.8 and 171.8-172.3°. The main components of the mixture were 2-chloronaphthalene-5-sulfonic acid (approx. 16%) and 2-chloronaphthalene-6,8-disulfonic acid (approx. 84%).

Experiment 5. The sulfonic acid mass obtained under the conditions of Experiment 1 (0.03 mole 2-chloronaphthalene) was held for 1460 hours at 20-25°. 1.21 g of the chloride from the 1st fraction of potassium salts 1.64 g was fractionally crystallized to give three fractions which were identified as 2-chloronaphthalene-6-sulfochloride (approx. 16%). The chloride (4.40, 0.69 and 1.26 g) from the 2nd, 3rd and 4th fractions of potassium salts (5.10, 0.78 and 2.37 g) was fractionally crystallized and identified as 2-chloronaphthalene-8-sulfochloride (approx. 84%).

Sulfonation of 2-chloronaphthalene-5-sulfonic acid. Experiment 6. To 14.7 g of 100% monohydrate (0.15 mole) was added 4.21 g of the anhydrous potassium salt of 2-chloronaphthalene-5-sulfonic acid (0.015 mole). Stirring at 20° was continued for 24 hours. Unchanged 2-chloronaphthalene-5-sulfonic acid was found after fractional crystallization of the chlorides (3.75 g) and of the anilides derived from them in all 8 fractions. This sulfonic acid remained unchanged also when its solution was heated in monohydrate of the above composition for 3 hours at 50°.

Experiment 7. To 28.79 g of 8.3% oleum (2.4 g free SO_3, 0.03 mole) was added 8.43 g anhydrous potassium salt of 2-chloronaphthalene-5-sulfonic acid. Stirring at 20° was continued for 22 hours. The 1st and 2nd fractions of potassium salts yielded 4.69 g chloride which was converted to the anilide. Fractional crystallization of the latter gave 9 fractions of the anilide of unchanged 2-chloronaphthalene-5-sulfonic acid (approx. 60%). The chloride (3.95 g) from the 3rd fraction of potassium salts was identified after fractional crystallization as pure 2-chloronaphthalene-5,7-disulfochloride (approx. 40%).

Sulfonation of 2-chloronaphthalene-1-sulfonic acid. Experiment 8. To 14.7 g 100% monohydrate (0.15 mole) was added 4.21 g anhydrous potassium salt of 2-chloronaphthalene-1-sulfonic acid (0.015 mole). Stirring at 20° was continued for 20 hours. Two fractions of potassium salts were obtained. The 1st fraction of potassium salts (2.69 g) was transformed into 2.10 g (approx. 54%) low-melting chlorides. The low-melting chloride less soluble in glacial acetic acid was converted to the anilide from which by fractional crystallization (from carbon tetrachloride) were obtained fractions with m. p. 137 and 134-135°; the melting points of mixtures with authentic 2-chloronaphthalene-1-sulfanilide were 137 and 134-135°. The chloride more soluble in glacial acetic acid had, after recrystallization, m. p. 130.5-131.5°; the mixture with 2-chloronaphthalene-8-sulfochloride had m. p.

131.7°. The 2nd fraction of potassium salts (4.99 g) was transformed into 2.28 g (approx. 42%) of low-melting chloride which was then converted to the anilide. After numerous recrystallizations (from carbon tetrachloride and benzene) the anilide had m. p. 237.5-238.5° (2-chloronaphthalene-1,5-disulfanilide, melting point of mixed specimen 239°). The mixture of products of sulfonation of 2-chloronaphthalene-1-sulfonic acid contained, apart from unchanged starting substance, 2-chloronaphthalene-8-sulfonic acid and 2-chloronaphthalene-1,5-disulfonic acid (approx. 40%).

SUMMARY

1. Sulfonation of 2-chloronaphthalene with monohydrate at 20° (for 3 hours) leads to 2-chloronaphthalene-8-sulfonic acid and a much smaller amount of 2-chloronaphthalene-5-sulfonic acid; the latter had not previously been detected in the products of sulfonation of 2-chloronaphthalene. When the sulfonation period is prolonged to 1460 hours, the reaction mass contains 2-chloronaphthalene-8-sulfonic acid and 2-chloronaphthalene-6-sulfonic acid.

2. Chloronaphthalene-5-sulfonic acid remains unchanged after treatment with monohydrate at temperatures up to 50°. Under the action of weak oleum at 20°, 2-chloronaphthalene-5-sulfonic acid is converted into 2-chloronaphthalene-5,7-disulfonic acid.

3. Sulfonation of the potassium salt of 2-chloronaphthalene-1-sulfonic acid with monohydrate at 20° gives 2-chloronaphthalene-1,5-disulfonic acid.

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D. I. Mendeleev Institute of Chemical Technology, Moscow.

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THE SULFONATION REACTION

XXXIX. THE HYDROLYSIS AND ISOMERIZATION OF NAPHTHALENE TRISULFONIC ACIDS

B. I. Karavaev and A. A. Spryskov

In spite of the great technical importance of naphthalene-1,3,6-trisulfonic acid, no systematic study of the hydrolysis and isomerization of trisulfonic acids of naphthalene has hitherto been undertaken. This is largely due to the lack of a method of quantitative determination of all the three isomeric trisulfonic acids formed by direct sulfonation of naphthalene. Hydrolysis of the 1,3,6-trisulfonic acid was observed by Lantz [1] at 180° in presence of 69.9-87.6% sulfuric acid. In another investigation Lantz [2] observed hydrolysis in presence of 64-96% sulfuric acid at 176-181°. The same paper described experiments in which isomerization of trisulfonic acids occurred. An attempt to attain equilibrium between the trisulfonic acids did not meet with success, since tetrasulfonic acid was formed under the conditions of most of the experiments.

In the present work we demonstrate the relative stability towards hydrolysis of the three isomeric trisulfonic acids at 161° and their isomerization at the same temperature in sulfuric acid solution. Mixtures were analyzed by the method previously described [3] which allows determination of the amount of 1,3,6-acid and of the sum of the 1,3,5-and 1,3,7-isomers.

EXPERIMENTAL

For determination of the relative stability towards hydrolysis of the isomers, a weighed sample of the free trisulfonic acid, containing hydrate water, was mixed in a test tube with the exactly determined amount of sulfuric acid, and the test tube was sealed off and heated in an Eyckman apparatus. The amount of trisulfonic acid hydrolyzed could be calculated from the increase in total acidity after heating (determined by volumetric method), or from the increase in the amount of sulfuric acid (determined gravimetrically).

Experiments were carried out in 75-78% sulfuric acid, since it had previously been found [4] that in 77% sulfuric acid at 160° disulfonic acids are not converted either into mono- or into trisulfonic acids; in the calculations we therefore assumed that hydrolysis goes to disulfonic acids.

The results of the experiments summarized in the Table show that the most labile isomer is the 1,3,5-acid, and the most stable one is the 1,3,7-acid. 1,3,6-Trisulfonic acid occupies an intermediate position. There is a very considerable difference between the stabilities of the 1,3,5- and the 1,3,7-isomers which is markedly reflected in the velocity of their isomerization.

Isomerization of all three naphthalene trisulfonic acids was performed in presence of 8-17 moles 96.1-110.3% sulfuric acid. 100% acid was used in experiments lasting up to 100 hours, but 96% acid was used when isomerization was carried out for 100 to 450 hours since prolonged heating with monohydrate leads to formation of a considerable amount of tetrasulfonic acid.

Oleum was added to a weighed sample of free trisulfonic acid, containing crystal water, in such quantity that after mixing the concentration of the sulfuric acid was close to 96 or 100%. Heating was effected continuously in sealed tubes at 161 ± 1°. At the conclusion of isomerization, the mixture was analyzed for its content of 1,3,6-acid and for total 1,3,5- and 1,3,7-trisulfonic acids by the previously described method [3].

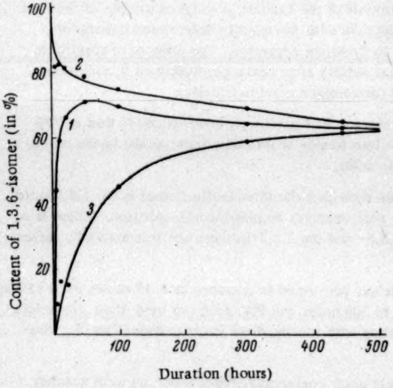
TABLE

Hydrolysis of Naphthalene Trisulfonic Acids at 161 ± 1°

Isomer	Amount of water (moles per mole sulfonic acid)	Duration of heating (hours)	% of sulfonic acids hydrolyzed (calculated on initial amount)
1,3,5-	5.28	10	52.6
1,3,6-	6.10	10	9.6
1,3,7-	5.25	10	0
1,3,5-	5.28	25	76.4
1,3,6-	6.10	25	15.2
1,3,7-	5.25	25	6.0
1,3,5-	5.28	35	84.1
1,3,6-	6.10	35	37.4
1,3,7-	5.25	35	14.2

Tetrasulfonic acid is absent from the reaction mixture after an isomerixation period of 300 hours, as was shown by a blank test in which the mixture was treated with chlorosulfonic acid and the chlorides dissolved in benzene. Identical results were obtained in isomerization carried out for 50 hours in presence of 96 and 100% sulfuric acid. This shows that the 100% acid does not give appreciable amounts of tetrasulfonic acid in 50 hours.

The plotted results of the experiments (see Diagram) show that isomerization of the 1,3,5-trisulfonic acid goes relatively quickly since after 10 hours the content of 1,3,6-isomer reaches 60%. The 1,3,7-acid is kinetically the most stable isomer. In harmony with conclusions previously reached by us [4], the velocity of its formation is evidently much lower than that of the velocity of formation of the 1,3,6-isomer, and this also leads predominantly to formation of the 1,3,6-isomer during isomerization of the 1,3,5-acid. The content of the 1,3,6-isomer reaches a maximum after 50-60 hours and then slowly falls, due to partial transformation into the kinetically more stable 1,3,7-isomer. The system tends toward an equilibrium which, however, is established with extreme slowness.



Isomerization curves of the trisulfonic acids. 1) 1,3,5-isomer, 2) 1,3,6-isomer, 3) 1,3,7-isomer.

Isomerization of the 1,3,6-acid goes very much more slowly, so that after 10 hours the content of 1,3,6-isomer falls to 82%. This is followed by a still slower change of composition with accumulation, evidently, of the 1,3,7-acid.

A state fairly close to equilibrium is reached in the above experiments. Thus, after isomerization for 446 hours, the 1,3,5-trisulfonic acid is transformed into a mixture containing 63.2% of the 1,3,6-isomer. The 1,3,6-acid was converted into a mixture containing 65.1% of 1,3,6-isomer, and the 1,3,7-acid into a mixture containing 61.5% 1,3,6-isomer. The isomerization curves of all three trisulfonic acids tend to converge in course of time. Extrapolation of the results justifies the conclusion that at the equilibrium state, which might be reached after 550-600 hours, the mixture will contain about 63% 1,3,6-acid and 37% 1,3,5- and 1,3,7-acids. Consequently, the 1,3,6-isomer, whose kinetic stability is intermediate between that of the other two isomers and which is more labile than the 1,3,7-isomer, is thermodynamically the most stable isomer since the velocity of its formation exceeds the velocity of formation of the 1,3,7-isomer. The lack of methods of individual determination of the 1,3,5- and the 1,3,7-acids prevents us from drawing a more precise picture of the composition of the mixtures formed on isomerization.

In the manufacture of 1,8-aminonaphthol-3,6-disulfonic acid, naphthalene is sulfonated with the objective of obtaining naphthalene-1,3,6-trisulfonic acid, and here the processes of isomerization of the trisulfonic acids play an important part. Applying the usual industrial method of sulfonation of naphthalene, we obtained the normal sulfonic acid mixture. Analysis of the latter showed that tetrasulfonic acid is absent and that the sum of the 1,3,5- and 1,3,7-acids is about 28%. In three specimens from different plant operations we likewise failed to find tetrasulfonic acid, and the content of the above trisulfonic acids was 27-28%. The 1,3,5- and 1,3,6-isomers are formed with higher velocity so that at the start the mixture contains only little of the 1,3,7-acid. In the subsequent course of the process the 1,3,5-isomer rearranges predominantly to the 1,3,6-acid, part of which in turn is slowly transformed into the 1,3,7-acid. Consequently, in the production of N-acid, the process of sulfonation should be interrupted as soon as the mixture contains the maximum amount of 1,3,6-isomer.

The conclusion of Fierz-David and Richter [5] that disulfonation "should be so conducted that mainly only the 1,6- and 2,7-acids are obtained, and therefore that the 1,3,6-acid is formed nearly quantitatively as the end product of sulfonation" is erroneous.

SUMMARY

The three isomeric naphthalene trisulfonic acids, formed by direct sulfonation of naphthalene, were subjected to hydrolysis at 161° in presence of 75-78% sulfuric acid. In resistance to hydrolysis the trisulfonic acids are in the order: 1,3,7- > 1,3,6- > 1,3,5-trisulfonic acid.

The three trisulfonic acids were subjected to isomerization at 161° in presence of 96 and 100% sulfuric acid. On starting from any given isomer, the system tends towards an equilibrium at which the content of 1,3,6-isomer is about 63%. Consequently, the thermodynamically most stable isomer is the 1,3,6-isomer, due to the higher velocity of its formation compared with that of the 1,3,7-isomer.

In the usual method of sulfonation of naphthalene to trisulfonic acid in the production of N-acid, the mixture is free from tetrasulfonic acid and about 72% of the 1,3,6-isomer is obtained.

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Invanov Institute of Chemical Technology

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SULFONIC ACIDS OF SULFONES AS BY-PRODUCTS OF SULFONATION REACTIONS

II. THE BEHAVIOR OF THE DISULFONIC ACID OF DIPHENYLSULFONE UNDER CONDITIONS OF ALKALINE FUSION OF BENZENE-m-DISULFONIC ACID

A. P. Shestov and N. A. Osipova

As was established by one of us [1], diphenylsulfone-3,3'-disulfonic acid invariably accompanies benzene-m-disulfonic acid; it was therefore of interest to study the behavior of this compound under the conditions of the alkaline fusion of benzene-m-disulfonic acid to form resorcinol.

Some of the investigators of the alkaline fusion of benzene-m-disulfonic acid reached the conclusions that this process is very complicated, that the yields of resorcinol are low (25 to 65%) and that the process of alkaline fusion is accompanied by a large number of secondary reactions [2]. Nevertheless a high yield (over 90%) of resorcinol has been reported [3] in the reaction starting from benzene-m-disulfonic acid.

Our purpose in the present work was to establish the degree of transformation of benzene-m-disulfonic acid into resorcinol during alkaline fusion, the possibility and degree of formation of resorcinol during alkaline fusion of diphenylsulfone-3,3'-disulfonic acid, and the influence of this impurity on the alkaline fusion of benzene-m-disulfonic acid.

The following precautions were taken to exclude secondary processes: we started from perfectly pure sulfonic acids (prepared from the corresponding sulfochlorides); the alkaline fusion was conducted in nickel capsules with complete exclusion of atmospheric oxygen. The specially designed appratus illustrated in the diagram was used.

The resorcinol in the melt was determined by nitrosation [4] and in some experiments by direct isolation. Phenol was also determined by bromination in the case of alkaline fusion of diphenylsulfone-3,3'-disulfonic acid.

The experiments established that benzene-m-disulfonic acid is nearly quantitatively converted into resorcinol. The yields on the starting sulfochloride are about 99%, and these yields are consistently maintained in all experiments (to within 0.1-0.2%). The very unfavorable effect of atmospheric oxygen was established. The yield was halved when the hermetic seal of the apparatus failed.

Diphenylsulfone-3,3'-disulfonic acid gave a yield of approximately 1 mole resorcinol per mole of sulfonic acid when the fusion was effected under the same conditions with a somewhat larger excess of alkali. This result was obtained on the basis of analysis by the nitrosation method. The amount of phenol found by bromination was 0.108 mole per mole of sulfonic acid.

Extraction with ether of the acidified solution of the melt, followed by chromatographic resolution of the ethereal solution on aqueous alumina, enabled the separation of an ethereal extract which, after evaporation of the ether, gave a product (m. p. 104-105°) containing 86% resorcinol in the amount of approximately 1 mole per mole of original sulfonic acid. Vacuum distillation followed by recrystallization from toluene gave resorcinol with the melting point reported in the literature. Phenol was identified in the form of the benzoyl derivative.

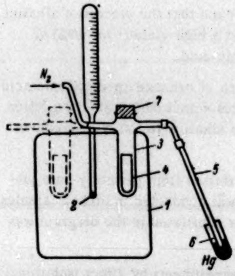
The considerable residue (about 1 mole, arbitrarily calculated on the phenol, per mole of sulfonic acid) remaining after separation of the resorcinol and phenol consisted of resins of a phenolic character (soluble in NaOH and insoluble in water). After freeing from resorcinol, these resins did not nitrosate under the usual conditions. This fact was evidence of the correctness of the analytical method of determination of resorcinol in the melts by nitrosation. We did not carry out further separation of the resins.

The fusion of diphenylsulfone-3,3'-disulfonic acid serves as proof of the structure of this compound. Since resorcinol is formed by the fusion, we can assume that at least one of the sulfo groups is in the meta-position to the SO_2 group. As we see from the literature data, no substantial rearrangement of sulfonic acids [5] occurs under the specified conditions of caustic fusion.

Mixtures of pure benzene-m-disulfonic acid and diphenylsulfone-3,3'-disulfonic acid for caustic fusion had the same molar ratios in which they could occur during sulfonation, i. e. from 60 : 40 to 95 : 5. The mixture of these sulfonic acids was fused with alkali in such a manner that 1 mole of each of the components gave substantially one mole of resorcinol (Table 2).

EXPERIMENTAL

The sodium salt of benzene-m-disulfonic acid was obtained by hydrolysis of the corresponding sulfochloride (m. p. 63°) in NaOH solution. The dry sodium salt was mixed with pulverized NaOH (or a mixture of NaOH and KOH), and the whole was transferred to a nickel capsule (see Diagram) which was placed in an electric furnace. The apparatus is fitted with side tubes, one of which connects to a nitrogen cylinder and the second (via a thick-walled capillary tube) to a mercury seal.



Apparatus for caustic fusion.
1) Thermostated furnace, 2) contact thermometer, 3) quartz test-tube, 4) nickel capsule, 5) thick-walled capillary tube, length 1 meter 6) mercury seal, 7) rubber stopper.

After completion of the fusion, the furnace was cooled; during this operation the mercury from the seal should rise along the tube; this is evidence of the tightness of the seal. The melt was extracted from the capsule with water under nitrogen, the resorcinol solution was analyzed by nitrosation and then extracted with ether.

The sodium salt of diphenylsulfone-3,3'-disulfonic acid was prepared from the sulfochloride of the acid (m. p. 180.5-181°) The procedure was similar to that described above.

In all experiments caustic fusion was carried out for 3 hours at 320°. The temperature was raised to 320° in 2-3 hours.

In the Tables below, benzene-m-disulfochloride is designated by m-DSC and diphenylsulfone-3,3'-disulfochloride by DPSC.

a) Alkaline fusion of the pure sodium salt of benzene-m-disulfonic acid. One gram of benzene-m-disulfochloride was fused, after saponification, with 3 g NaOH (20 moles NaOH per mole sulfo salt). 0.3954 g resorcinol was found in the melt by nitrosation. The resorcinol yield in the melt was 99.01%. By ether extraction a product with m. p. 105-105.6° and containing 95.25% resorcinol was obtained. The remaining experiments of this series were carried out in a similar fashion.

b) Caustic fusion of the pure sodium salt of diphenylsulfone-3,3'-disulfonic acid. A larger excess of alkali was taken in this series of experiments because of the pure sodium salt of the acid is a very fluffy powder, poorly miscible with alkali, and the melt catches fire with a small excess of alkali.

In Experiment 11 (Table 1) the acidified solution of the melt was filtered off from resinous impurities and the phenol was distilled off with steam; the main solution was extracted with ether and the latter was passed through aqueous alumina. The resorcinol was completely washed out of the column by elution with ether. The ethereal solution was repeatedly purified by passing through the column and then evaporated to give 5.95 g resorcinol with m. p. 104-105° and a resorcinol content of 85.9%. Distillation in vacuum followed by crystallization from toluene gave a product with m. p. 110-110.5° (the literature reports m. p. 110°).

TABLE 1

Experiment No.	Taken for fusion			Resorcinol determined by nitrosation (in g)	Theoretical yield of resorcinol (g)*
	DPSC (in g)	NaOH (in g)	moles NaOH per mole sulfo salt		
6	1.0000	10	25	0.2843	0.2650
8	1.0000	15	37.5	0.2460	0.2650
11	20.0000	200	25	5.3000	5.3000

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* On the assumption that 1 mole diphenylsulfone-3,3'-disulfonic acid gives 1 mole resorcinol.

TABLE 2

Experiment No.	Taken for fusion (in g)		Theoretical yield of resorcinol from fusion (in g)*			Resorcinol determined by the nitrosation method (in g)	Yield of resorcinol (in %)
	m-DSC	DPSC	m-DSC	DPSC	mixture of chlorides		
12	0.7313	0.3679	0.2924	0.0974	0.3898	0.3898	100.0
14	0.8000	0.2010	0.3198	0.0532	0.3731	0.3660	98.11
16	0.8000	0.1065	0.3198	0.0282	0.3480	0.3474	99.83
18	0.9000	0.0755	0.3598	0.0200	0.3798	0.3793	99.87
20	0.9500	0.0378	0.3798	0.0100	0.3898	0.3891	99.81

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* On the assumption that 1 mole chloride gives 1 mole resorcinol.

Found %: C 65.2; H 5.41. $C_6H_6O_2$. Calculated %: C 65.45; H 5.49.

0.49 g phenol was found in the phenolic liquor by bromination and was identified as the benzoyl derivative. Recrystallization from methyl alcohol gave a product with m. p. 66-66.5° (literature 66°). A mixture with pure benzoyl derivative of phenol did not exhibit a melting point depression.

Found %: C 79.26; H 5.04. $C_{13}H_{10}O_2$. Calculated %: C 78.75; H 5.08.

A resinous residue was obtained after treatment of the alumina with methyl alcohol and distilling off the solvent. Total resin collected was 2.69 g. After passage through a column and freeing from resorcinol, the resin failed to nitrosate under the usual conditions of analysis.

c) Alkaline fusion of a mixture of pure sodium salts of benzene-m-disulfonic acid and diphenylsulfone-3,3'-disulfonic acid. The mixture was fused under the same conditions as for the separate components (m. p. 320°, held for 3 hours, amount of alkali 12-18 moles calculated per mole of benzene; in Experiment 14 of Table 2 there were 18.5 moles per mole of benzene, in the remaining experiments 11.5-12 moles were taken per mole of benzene).

SUMMARY

1. The alkaline fusion of benzene-m-disulfonic acid goes easily and completely to give a 98.6-99.0% conversion to resorcinol.

2. Diphenylsulfone-3,3'-disulfonic acid, which invariably accompanies benzene-m-disulfonic acid, gives approximately 1 mole resorcinol per mole when fused with alkali. The remaining portion of the diphenylsulfone-3,3'-disulfonic acid molecule is converted into condensed high-molecular phenols of a resinous character and a very small proportion into ordinary phenol.

3. Fusion of mixtures of benzene-m-disulfonic acid and diphenylsulfone-3,3'-disulfonic acid with alkali leads to the same results as fusion of the individual components – each compound gives 1 mole resorcinol per mole.

4. A precision method of alkaline fusion is developed which gives consistent and nearly quantitative yields.

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K. E. Voroshilov Institute of Research
on Organic Intermediates and Dyes.

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TRICHLOROPHOSPHAZOTRICHLOROACETYL AND THE ACID CHLORIDE OF THE N-PHOSPHORIC ACID OF TRICHLORIMINOACETYL CHLORIDE

A. V. Kirsanov and G. L. Derkach

During a study of the reaction of phosphorus pentachloride with trichloroacetamide, Wallach [1] obtained a compound of the composition C_2OCl_6NP and assigned to it, without adequate experimental proof, the structure $CCl_3CCl{=}NPOCl_2$ (I), i. e. the acid chloride of the N-phosphoric acid of trichloriminoacetyl chloride. Wallach explained the formation of (I) by the following scheme, again without adequate experimental support:

$$CCl_3CONH_2 + PCl_5 \longrightarrow CCl_3CCl_2NH_2 + POCl_3,$$

$$CCl_3CCl_2NH_2 \longrightarrow HCl + CCl_3CCl{=}NH,$$

$$CCl_3CCl{=}NH + POCl_3 \longrightarrow HCl + CCl_3CCl{=}NPOCl_2 \text{ (I)},$$

Steinkopf later studied [2] the reaction of phosphorus pentachloride with some halo-, halonitro- and haloalkyl-acetamides and obtained compounds analogous to (I). To all his compounds Steinkopf, like Wallach, assigned the structure $RCCl{=}NPOCl_2$, again without sufficient proof.

Data have come to light in recent years which cause doubt to be thrown upon the validity of the structure $RCCl{=}NPOCl_2$ for compounds formed from carboxylic acid amides, not substituted at the nitrogen, and phosphorus pentachloride. It was found that the following single reaction scheme is applicable to unsubstituted amides of sulfonic acids [3], amides of carbonic acid [4], esters of oxamic acid [5] and amides of aromatic carboxylic acids [6]:

$$AcNH_2 + PCl_5 \longrightarrow 2HCl + AcN{=}PCl_3,$$

i. e. the corresponding trichlorophosphazo compounds are formed. It was shown in addition that the reaction $RCN + HCl + POCl_3$ or $RCCl{=}POCl_3$ does not go [4]. Consequently there are good grounds for assuming that the reaction of phosphorus pentachloride with trichloroacetamide goes with formation not of a derivative of trichloriminoacetyl (I) but with formation of a derivative of trichloroacetamide, namely, trichlorophosphazotrichloroacetyl (II), in accordance with a general scheme, i. e.

$$CCl_3CONH_2 + PCl_5 \longrightarrow 2HCl + CCl_3CON{=}PCl_3 \text{ (II)}.$$

In the present work we have succeeded in fully and strictly proving by chemical methods the structure of substances obtained by reaction of phosphorus pentachloride with unsubstituted amides of substituted acetic acids. The particular compound whose structure was established was the product of interaction of phosphorus pentachloride with trichloroacetamide. For the sake of brevity this substance will now be referred to as product A.

Treatment of product A with water or, better, with 1 mole of anhydrous formic acid, gives a very good yield of the acid chloride of N-trichloroacetylamidophosphoric acid. The structure of the latter is not in doubt at all, but its formation is no guide to the structure of product A since substances of either structure (I) or structure (II) have one particularly easily hydrolyzable chlorine atom and therefore the action of 1 mole formic acid must lead to one and the same product, according to the schemes:

$$\left.\begin{array}{l}CCl_3CCl{=}NPOCl_2\ (I) + HCOOH \\ CCl_3CON{=}PCl_3\ (II) + HCOOH\end{array}\right\rangle CO + HCl + CCl_3CONHPOCl_2.$$

Phosphorus pentachloride acts on the acid chloride of N-trichloroacetyl-amidophosphoric acid to give a product B (isomeric with product A) in quantititative yield. The reaction goes with considerably greater difficulty at higher temperature and for a longer period – than the reaction of phosphorus pentachloride with trichloroacetamide, and it quantitatively goes according to the scheme:

$$CCl_3CONHPOCl_2 + PCl_5 \longrightarrow HCl + POCl_3 + C_2OCl_6NP.$$

Absorption of heat is not observed during the reaction although heat is absorbed in the reaction of phosphorus pentachloride with amides of carboxylic acids and sulfonic acids [3, 6]. The reaction goes under conditions similar to the conditions of the reaction of phosphorus pentachloride with dimethylamides of carboxylic acids [7], i. e. when the "carbonyl" oxygen of the carboxylic acid amide undoubtedly exchanges with chlorine according to the scheme:

$$C_6H_5CON(CH_3)_2 + PCl_5 \longrightarrow CH_3Cl + POCl_3 + C_6H_5CCl{=}NCH_3.$$

The structure of (I) must therefore be assigned to product B, and its formation can be represented by the following scheme:

$$CCl_3CONHPOCl_2 + PCl_5 \longrightarrow POCl_3 + HCl + CCl_3CCl{=}NPOCl_2.$$

It can consequently be considered proved that the action of phosphorus pentachloride on substituted acetamides gives the corresponding trichlorophosphazo compounds and not derivatives of iminoacids.

The substances obtained by Wallach [1] and Steinkopf [2] and described by them as compounds of the type of $RCCl{=}NPOCl_2$, where $R = CCl_3$, $CHCl_2$, CBr_3, CCl_2NO_2, etc., are actually trichlorophosphazo compounds, i. e. compounds of the type of $RCON{=}PCl_3$.

Trichlorophosphazotrichloroacetyl (product A) differs markedly in physical and chemical properties from its isomer, the acid chloride of the N-phosphoric acid of trichloroiminoacetyl chloride (product B). Product A melts at 77-79° and product B at 40-41°; a mixed sample melts at 25-56°. Product B is very much more soluble in the majority of organic solvents than product A. Product B, as the acid chloride of an iminoacid, hydrolyzes with considerably greater facility than product A which is a trichlorophosphazo compound. Formolysis of both compounds with 1 mole formic acid gives one and the same acid chloride of N-trichloroacetylamidophosphoric acid (see scheme above).

Nearly all the trichlorophosphazoacyls known up to now quantitatively break down to phosphorus oxychloride and nitriles when heated at a little higher than their melting point [4, 6]. Trichlorophosphazotrichloroacetyl is considerably more stable and can be distilled at atmospheric pressure with insignificant decompoisition. Consequently, neither Wallach [1] nor Steinkopf [2] observed that heating of trichlorophosphazotrichloroacetyl goes with thermal breakdown with formation of trichloroacetonitrile and phosphorus oxychloride according to the general scheme of thermal breakdown of trichlorophosphazo compounds:

$$RCON{=}PCl_3 \longrightarrow POCl_3 + RCN\ [4, 6],$$

$$ClSO_2N{=}PCl_3 \longrightarrow POCl_3 + ClSON\ [8].$$

The thermal breakdown of trichlorophosphazotrichloroacetyl at 260° is completed in 3 hours with a yield of 89.4 % (calculated on the phosphorus oxychloride) and of 59.4% (calculated on the trichloroacetonitrile). The yield on the phosphorus oxychloride is undoubtedly closer to the true yield of thermal decomposition because trichloroacetonitrile undergoes secondary processes of polymerization under the drastic conditions of reaction and forms nonvolatile products. The thermal stability of trichlorophosphazotrichloroacetyl is probably the consequence of the large positive charge on the carbon atom of the CCl_3 group and the resultant reduced polarization of the C= O bond of the $CON=PCl_3$ group.

As in the case of trichlorophosphazoacyls of the aromatic series [4, 6], the thermal cleavage of trichlorophosphazotrichloroacetyl goes with greater facility in presence of hydrogen chloride. The reaction temperature drops to 210° and the duration to 2 hours 15 minutes, while the yields are slightly higher. The catalytic effect of hydrogen chloride, however, is considerably lower than for trichlorophosphazoacyls of the aromatic series [4, 6], and this, too, is probably the consequence of the reduced polarization of the C= O bond (hindrance to addition of hydrogen chloride with formation of an intermediate product).

Thermal cleavage of product B leads to formation of phosphorus oxychloride and trichloroacetonitrile according to the scheme:

$$CCl_3CCl{=}NPOCl_2 \longrightarrow POCl_3 + CCl_3CN,$$

i. e. with translocation of a chlorine atom. Cleavage goes at 220° and is completed in the course of 1 1/2 hours, i. e. at a lower temperature and in a shorter time than for product A. The yields of phosphorus oxychloride (82.0%) and trichloroacetonitrile (53.2%), however, are very much lower than in the case of product A. Consequently, it is impossible to decide which atom more easily migrates to the phosphorus – the oxygen or the chlorine. The lower yield from the thermal cleavage of product B indicates the improbability of preliminary isomerization of product A to product B. Evidently both product A and product B undergo thermal cleavage without preliminary isomerization into one another.

Both product A and product B easily react with alcohols, phenols, amines, atc. and are therefore valuable starting substances for the preparation of diverse derivatives of phosphoric acid of new types.

EXPERIMENTAL

The preparation, isolation and recrystallization of all the substances described in the present paper are carried out under conditions excluding as far as possible the action of atmospheric moisture. All solvents are used solely in the dry state.

Preparation of trichlorophosphazotrichloroacetyl $CCl_3ON=PCl_3$ (product A). A mixture of 0.5 mole trichloroacetamide, 80 ml carbon tetrachloride and 0.515 mole pulverized phosphorus pentachloride was heated at 70-75° until no more hydrogen chloride was evolved; this required 30-40 minutes. The solvent was driven off in vacuum at 70°. The residue was crude trichlorophosphazotrichloroacetyl which set to a solid crystalline mass on cooling. Yield 99.7% (148.6 g). The product was recrystallized from 160 ml ligroine (b. p. 80-90°). The yield of perfectly pure substance (stout, colorless, transparent prisms) was 90.6% (135.0 g); it is very slowly hydrolyzed by moisture of the air; m. p. 77-79° in agreement with the literature [1, 2].

Preparation of the acid chloride of N-trichloroacetylamidophosphoric acid, $CCl_3CONHPOCl_2$. To a solution of 0.2 mole product A (59.6 g) in 150 ml benzene was added 0.2 mole anhydrous formic acid (9.2 g). A fairly violent reaction commenced immediately and continued for 30-40 minutes. After 24 hours the crystals (fine needles) were drained, washed twice (5 ml each time) with benzene, and dried in vacuum at 60°. The filtrate was evaporated to one third of its volume and the crystals were collected. Total yield 87.7% (49.0 g), m. p. 148-150° in agreement with the literature [1, 2].

Preparation of the acid chloride of the N-phosphoric acid of trichloroiminoacetylchloride, $CCl_3CCl=NPOCl_2$ (product B). 0.1 mole acid chloride ot trichloroacetylamidophosphoric acid (27.9 g) was carefully mixed with 0.1 mole phosphorus pentachloride, and the mixture was heated until hydrogen chloride ceased to come off. On the boiling water bath the reaction was completed in 2 hours, at 115-120° (glycerol bath) in 15-20 minutes.

During the reaction 99-101% (0.099-0.101 mole) hydrogen chloride was released and was collected and determined by the usual methods. The reaction product was a colorless mobile liquid – a mixture of phosphorus oxychloride and product B; yield 100.0% (45.2 g). The phosphorus oxychloride was distilled off in vacuum (6-7 mm) at 40-50° (40-50 minutes). Product B in the residue (colorless liquid) crystallized completely on cooling; yield 100.0% (29.8 g), m. p. 37-41°. The product was purified by recrystallization from 10 ml ligroine (washed with 0.5 ml ligroine) and dried in vacuum at room temperature. Yield 57.1% (17.0 g), m. p. 40-41°. Another 10% perfectly pure substance could also be separated from the mother liquor. Product B can be used for preparative purposes without recrystallization, since the "crude" product is sufficiently pure and melts only 3° lower than the recrystallized substance.

The acid chloride of the N-phosphoric acid of trichloroiminoacetyl chloride (product B) is a colorless substance, crystallizing in the form of long platelets, reacting with facility with water, alcohols, phenols, amines and other substances containing active hydrogen atoms. In the air product B hydrolyzes very easily, becomes waxlike and then deliquesces. A mixture of products A and B melts unsharply at 25-26°. Product B is readily soluble in benzene, carbon tetrachloride, ether, acetone, chloroform, and dioxane, and with rather more difficulty in ligroine. Recrystallization of product B is therefore bound up with great losses (see above).

Found %: N 4.83; hydrolyzable Cl 35.8. Acid equivalent after hydrolysis 4.94, 4.93. C_2OCl_6NP.

Calculated %: N 4.69; hydrolyzable Cl 35.7; acid equivalent after hydrolysis 5.00.

Preparation of the acid chloride of N-trichloroacetylamidophosphoric acid from product B. To a solution of 0.01 mole product B (2.98 g) in 50 ml benzene was added 0.01 mole anhydrous formic acid (0.46 g). After 24 hours, the crystals were collected, washed with benzene and dried. The mother liquor was evaporated to a small volume and the separated substance was collected. Total yield of acid chloride of N-trichloroacetylamidophosphoric acid 91.2% (2.4 g), m. p. 148-150°; no depression of melting point in mixed test with authentic acid chloride of N-trichloroacetylamidophosphoric acid.

Thermal cleavage of trichlorophosphazotrichloroacetyl (product A). 0.15 mole of product A (44.7 g) was placed in a 100 ml of two-necked flask connected to a fractionating column 100 mm long, a straight condenser and a receiver, and the substance was gradually heated on a metal bath. In the second neck of the flask was inserted a stopper with a thermometer whose bulb was immersed in the substance. At 220-225° decomposition commenced and proceeded very slowly; the process intensified at 260°. The resultant mixture of phosphorus oxychloride and trichloroacetonitrile was distilled off at a vapor temperature of 86-87°. After 3-hours' heating at 260°, decomposition came to an end; the flask contained 21% (9.4 g) of a black carbonized mass; the distillate was a transparent, colorless liquid with an acrid odor – a mixture of phosphorus oxychloride and trichloroacetonitrile. The distillate was redistilled in a 250 mm fractionating column to give 59.4% (12.9 g) of trichloroacetonitrile with b. p. 85-87° and 89.4% (21.6 g) of phosphorus oxychloride; the two substances were identified by the usual tests. Experimental losses 1.8% (0.8 g).

Thermal cleavage of trichlorophosphazotrichloroacetyl in presence of hydrogen chloride. The procedure was the same as before except that a very slow stream of dry hydrogen chloride was passed through during the whole period (one bubble every 2-3 seconds). Decomposition commenced at 205° and went with satisfactory speed at 210°. The reaction was completed in 2 1/4 hours at 210°. The amount of carbonized residue was 13.4% (6.0 g), that of trichloroacetonitrile was 76.8% (16.7 g) and that of phosphorus oxychloride was 91.2% (21.0 g); experimental losses were 2.2% (1.0 g).

Thermal cleavage of product B. The procedure was the same as with product A. Cleavage commenced at 200°, went with satisfactory speed at 220° and was complete after 1 1/2 hours. Yield of carbonized residue 28.8% (12.9 g), of trichloroacetonitrile 53.3% (11.55 g), of phosphorus oxychloride 82.0% (18.9 g); experimental loss 3.0% (1.35 g).

SUMMARY

1. Reaction of phosphorus pentachloride with trichloroacetamide gives trichlorophosphazotrichloroacetyl and not the acid chloride of the N-phosphoric acid of trichloroiminoacetyl chloride, as was thought up to now.

2. Acid chloride of the N-phosphoric acid of trichloroiminoacetyl chloride itself was obtained by the action of phosphorus pentachloride on the acid chloride of N-trichloroacetylamidophosphoric acid.

3. Substances obtained by Wallach [1] and Steinkopf [2] from phosphorus pentachloride and amides of substituted acetic acids and described by them as compounds of the type of $RCCl=NPOCl_2$ are actually compounds of the type of $RCON=PCl_3$.

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Dnepropetrovsk Institute of Metallurgy

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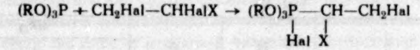
THE MECHANISM OF THE ARBUZOV REARRANGEMENT

III. REACTION OF THE NITRILE AND METHYL ESTER OF α, β-DIBROMO- AND α, β-DICHLOROPROPIONIC ACID WITH PHOSPHITES

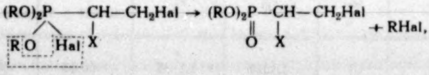
V. S. Abramov and N. A. Ilyina

We previously reported [1, 2] that the Arbuzov rearrangement of aliphatic phosphites under the action of α, β-dihaloethyl alkyl and monohalomethyl alkyl esters goes in two separate and independent steps. In the first step an intermediate addition compound is formed; although it was not isolated in the chemically pure form, its existence was proved by the course of the reaction and the transformations. In the second step the intermediate addition compound is decomposed by heat to form alkyl halide and ester of alkylphosphinic acid.

It was possible to follow the separate courses of the Arbuzov rearrangement of aliphatic phosphites because the reaction was conducted with halo derivatives in which the halogen atom is readily mobile and easily enters into reaction. The reactions were performed at room temperature at which the addition compounds do not break down. It may be expected that the Arbuzov rearrangement with other active halo derivatives would likewise go in two separate steps. We investigated the reactions of the nitrile (I) and the methyl ester (II) of α, β-dibromopropionic acid and the nitrile (III) and methyl ester (IV) of α,β-dichloropropionic acid with the ethyl (V) and butyl (VI) esters of phosphorous acid. The reaction may be represented thus:



$$(RO)_3P + CH_2Hal{-}CHHalX \rightarrow (RO)_3\underset{Hal}{\underset{|}{P}}{-}\underset{X}{\underset{|}{CH}}{-}CH_2Hal \qquad (1)$$



$$\underset{\boxed{RO\quad Hal}}{(RO)_2P}{-}{-}\underset{X}{\underset{|}{CH}}{-}CH_2Hal \rightarrow (RO)_2\underset{O}{\underset{\|}{P}}{-}\underset{X}{\underset{|}{CH}}{-}CH_2Hal + RHal, \qquad (2)$$

R is C_2H_5 or C_4H_9; Hal is Cl or Br, and X is CN or $COOCH_3$.

The experiments showed that the course of the reaction of methyl α,β-dibromopropionate with triethyl phosphite and tributyl phosphite is similar to that with α,β-dihaloethylalkyl esters, i. e. in two separate steps as is confirmed by the gradual change in physical constants of the reaction mixture at room temperature. When the reaction comes to an end, the constants no longer change, and this occurs approximately after 3-4 days. The change in constants is shown in Table 1.

The volume of the reaction mass increases in the reaction of methyl α,β-dibromopropionate with triethyl and tributyl phosphite because the specific gravity progesssively decreases (Table 1). Quantitative measurements of the volume change in the dilatometer showed a volume increase of 2.0% in 25 hours in the reaction of methyl α,β-dibromopropionate with triethyl phosphite and an increase of 1.6% in 31 hours in reaction with tributyl phosphite.

Methyl α,β-dichloropropionate does not react with triethyl phosphite or tributyl phosphite at room temperature and with heating to 60°. The starting substances are recovered on fractionation in vacuum. Kamai and Kukhtin [3] studied the action of methyl α,β-dichloropropionate on phosphites at 100 and 120°.

α,β-Dibromopropionitrile and α,β-dichloropropionitrile react with extraordinary facility with triethyl phosphite and tributyl phosphite. Considerable heat is developed. In one experiment, when 25.0 g triethyl phosphite and 21.3 g α,β-dibromopropionitrile were run together while being cooled to −12°, the reaction went explosively and the reaction mass was thrown out of the flask. Subsequent experiments were conducted with addition of the phosphite to α,β-dibromopropionitrile and α,β-dichloropropionitrile in small portions and with cooling in a freezing mixture. As we see from Table 1, the reaction between phosphites and α,β-dibromo- and dichloropropionitriles goes very quickly: the constants, determined immediately after mixing of the reactants, do not change any further.

TABLE 1

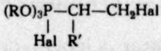
Change of Constants of Reaction Products with Time

Reacting substances	Immediately after mixing		Final values	
	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}
(II) + (V)	1.4610	1.3949	1.4390	1.3618
(II) + (VI)	1.4500	1.2522	1.4435	1.2481
(III) + (V)	1.4310	1.1334	1.4310	1.1335
(I) + (V)	1.4370	1.3230	1.4370	1.3230
(III) + (VI)	1.4280	1.0333	1.4280	1.0333
(I) + (VI)	1.4435	1.1972	1.4438	1.1972

It is not possible to isolate the addition products in the chemically pure form. As previously reported, they do not crystallize on cooling. The molecular refractions were calculated from the final constants(Table 2).

TABLE 2

Constants of Addition Products of the General Formula



$$(RO)_3P-\underset{Hal}{CH}-\underset{R'}{CH}-CH_2Hal$$

R	R'	Hal	n_D^{20}	d_4^{20}	MR_D	
					found	calculated
C_2H_5	CN	Cl	1.4310	1.1335	66.23	68.33
C_2H_5	CN	Br	1.4370	1.3230	75.05	74.07
C_2H_5	$COOCH_3$	Br	1.4390	1.3620	79.68	78.23
C_4H_9	CN	Cl	1.4380	1.0333	95.02	96.04
C_4H_9	CN	Br	1.4440	1.1972	102.83	101.84
C_4H_9	$COOCH_3$	Br	1.4435	1.2480	105.47	105.94

The addition products were decomposed by heating in accordance with equation (2). The corresponding alkyl halide was split off in very good yield. The conditions of thermal decomposition of the addition compounds and the yields of alkyl halides are given in Table 3.

A small fraction with a different boiling point is obtained apart from the halo derivatives, in the decomposition of the products of addition of dibromopropionic acid derivatives to phosphites. For example, careful fractionation of the products of decomposition of the complex (II + VI) in a Widmer column gave a small quantity of product with b. p. 80-83° and n_D^{20} 1.4100, whose constants agreed with those of methyl acrylate. Formation of the latter may be due to cleavage of a molecule of bromine from methyl α,β-dibromopropionate. Tributyl phosphite functions here as a dehalogenating agent. The reaction may be represented by the scheme:

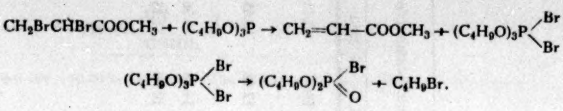
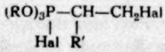


TABLE 3

Conditions of Thermal Decomposition of Addition Products of the General Formula



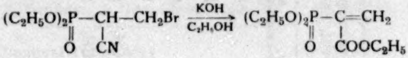
$$(RO)_3P-\underset{Hal}{\underset{|}{C}}H-\underset{R'}{\underset{|}{C}}H_2Hal$$

R	R'	Hal	Bath temperature	Yield of alkyl halide (%)
C_2H_5	CN	Cl	80— 90	98.5
C_2H_5	CN	Br	80— 90	93.4
C_2H_5	$COOCH_3$	Br	80— 90	88.7
C_4H_9	CN	Cl	110—130	76.0
C_4H_9	CN	Br	130—140	96.5
C_4H_9	$COOCH_3$	Br	130—140	84.6

Such a course of reaction of phosphites with dihalo derivatives was first observed by B. A. Arbuzov and B. P. Lugovkin [4] who reacted dibromostyrene with triethyl phosphite at 150-160° and isolated styrene from the reaction products.

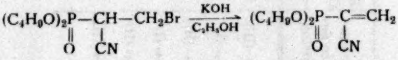
The residue after decomposition was vacuum-distilled. It was impossible, however, to fractionate the products because decomposition occurred with transformation of the flask contents into a dark resin. After several unsuccessful attempts to obtain the esters of α-cyano-β-haloethyl phosphinic acid or esters of α-phosphono-β-bromopropionic acid, we made a different approach to the problem. We treated the crude residue with alcoholic potassium hydroxide in order to split off hydrogen halide and obtain the corresponding unsaturated compounds.

Cleavage of hydrogen halide from cyano derivatives of ethylphosphinic acid was accompanied by saponification of the nitrile group to carboxyl and formation of the ethyl ester of α-ethoxyphosphonacrylic acid.



$$(C_2H_5O)_2\underset{O}{\underset{\|}{P}}-\underset{CN}{\underset{|}{C}}H-CH_2Br \xrightarrow[C_2H_5OH]{KOH} (C_2H_5O)_2\underset{O}{\underset{\|}{P}}-\underset{COOC_2H_5}{\underset{|}{C}}=CH_2$$

Cleavage of hydrogen halide from the cyano derivatives of butylphosphinic acid gave the normal, nitrogen-containing substances.

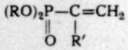


$$(C_4H_9O)_2\underset{O}{\underset{\|}{P}}-\underset{CN}{\underset{|}{C}}H-CH_2Br \xrightarrow[C_2H_5OH]{KOH} (C_4H_9O)_2\underset{O}{\underset{\|}{P}}-\underset{CN}{\underset{|}{C}}=CH_2$$

The degree of unsaturation of the butyl ester of cyanovinylphosphinic acid could not be satisfactorily determined. The unsaturation was determined both by direct addition of bromine and by the bromide-bromate method. H. Meyer cites a reference [5] to the effect that some unsaturated substances do not add on halogens. Bromine

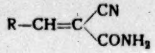
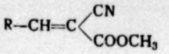
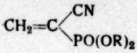
TABLE 4

Formation and Constants of Esters of α-Substituted Vinylphosphinic Acids



$$\underset{\substack{\| \\ O}}{(RO)_2P}-\underset{\substack{| \\ R'}}{C}=CH_2$$

Product subjected to decomposition	Residue from decomp. of $(RO)_2\underset{\substack{\| \\ O}}{P}-\underset{\substack{| \\ R'}}{CH}-CH_2$ Hal.			Substance obtained		Boiling point and pressure (mm)	n_D^{20}	d_4^{20}	MR_D		Yield (in %)	Phosphorus content (%)	
	R	R′	Hal	R	R′				found	calc.		found	calc.
(V) + (III)	C_2H_5	CN	Cl	C_2H_5	$COOC_2H_5$	99—100° (17)	1.4114	1.0684	54.90	55.98	44.2	13.30, 13.08	13.13
(V) + (I)	C_2H_5	CN	Br	C_2H_5	$COOC_2H_5$	102—103 (19)	1.4112	1.0725	54.67		21.0	— —	—
(VI) + (III)	C_4H_9	CN	Cl	C_4H_9	CN	136—138 (15)	1.4205	1.0006	62.07	65.73	30.0	12.65, 12.42	12.65
(VI) + (I)	C_4H_9	CN	Br	C_4H_9	CN	135—138 (15)	1.4208	1.0018	61.99		23.0	— —	—
(V) + (II)	C_2H_5	$COOCH_3$	Br	C_2H_5	$COOCH_3$	66—68 (5)	1.4130	1.0955	50.53	51.37	16.9	14.09, 14.30	13.96
(VI) + (II)	C_4H_9	$COOCH_3$	Br	C_4H_9	$COOCH_3$	125—126 (5)	1.4205	1.0143	69.45	69.84	20.7	11.12, 10.90	11.15

uaually does not add on if the olefinic hydrocarbon atoms are linked with highly negative groups. For example, compounds containing the  $R{-}CH{=}C\begin{smallmatrix}CN\\CONH_2\end{smallmatrix}$ or  $R{-}CH{=}C\begin{smallmatrix}CN\\COOCH_3\end{smallmatrix}$ group only give bromine-substituted compounds under the action of bromine. The unsaturated compounds  $CH_2{=}C\begin{smallmatrix}CN\\PO(OR)_2\end{smallmatrix}$ that we prepared are similar to those cited.

The esters of *a*-cyanovinylphosphinic acid and the esters of *a*-phosphonacrylic acid distil to leave an insignificant residue; their constants are presented in Table 4.

Esters of *a*-sutstituted vinylphosphinic acid were also previously prepared [2, 6].

Unsaturated phosphorus-containing compounds were synthesized with the objective of converting them into high-molecular compounds. Although the prepared esters had a polar character (as previously described), they did not polymerize to high-molecular compounds, probably due to steric hindrance.

The experimental studies were performed by the usual methods, as already described [1].

SUMMARY

1. Methyl *a*,*β*-dibromopropionate reacts with triethyl and tributyl phosphite with formation of an intermediate addition compound, as is confirmed by the change of the physical constants of the reacting products. The Arbuzov rearrangement goes in two separate and independent steps.

2. The nitriles of *a*,*β*-dichloro- and *a*,*β*-dibromopropionic acids react with remarkable violence with triethyl and tributyl phosphite. In these cases also, we must assume the formation of intermediate addition compounds, as indicated by subsequent reactions.

3. Methyl and ethyl esters of nitriloethoxy- and butoxy-*a*-phosphonacrylic acids are obtained. They do not polymerize under the usual conditions.

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Kazan S. M. Kirov Institute of Chemical Technology

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[illegible] does not add on to the [illegible] with [illegible]. For example,

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The rates of [illegible] are presented in Table 4.

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CONCLUSIONS

1. [illegible]

2. The [illegible]

3. [illegible]

LITERATURE CITED

(1) [illegible]

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Kazan S. M. Kirov Institute of Chemical Technology Received [illegible]

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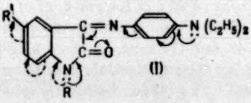
AZOMETHINE DYES FROM OXINDOLE DERIVATIVES. II

M. S. Kisteneva

In the previous communication [1] we had examined the influence of various substituents, found on the nitrogen atom of the hetero radical (R), on the color of the azomethine dyes from oxindole (I) (R' = H) derivatives; Here it was established that the introduction of an electronegative group in the 1 position causes a deepening of the color of these compounds, while the presence of an electropositive group on the nitrogen atom leads to a slight shift in the position of the absorption maximum of the dyes toward the short-wave side of the spectrum. Apparently, these phenomena are associated with a change in the electron shifts along the conjugation chain (from the diethylamino group to the carbonyl oxygen of the oxindole radical). The presence of an electronegative group in the 1 position facilitates a more uniform distribution of the electron density in the chromophore, since it weakens the reaction between the nitrogen of the hetero radical and carbonyl oxygen. The introduction of an electropositive group or nitrogen of the hetero radical should enhance the electron shifts from this atom to the carbonyl oxygen, in connection with which the electron density in the chromophore becomes less uniform.

It seemed of interest to study the dependence of color of such dyes on the presence of different substituting groups in the benzene ring, and also the reciprocal influence on color of the substituents with a nitrogen atom also present in the aromatic ring. In connection with this we synthesized a number of oxindole derivatives with substituents in the 5 position, a part of which also contained an alkyl, phenyl or acetyl group on the nitrogen atom of the hetero radical. The condensation of these compounds with p-nitrosodiethylaniline gave the corresponding azomethine dyes (I):



(I)

where : R = H, CH_3, C_2H_5, C_6H_5, $COCH_3$; R' = CH_3, OH, OCH_3, NO_2, $NHCOCH_3$ and Br.

The dyes of this group, the same as those not containing substituents in the benzene ring, have one fairly wide absorption band in the visible portion of the spectrum.

The positions of the absorption maxima of the synthesized (3)-isatin p-diethylaminoanils in alcohol solutions are given in Table 1.

As can be seen from the data in Table 1, the presence of a weakly electropositive group (CH_3, OH, OCH_3, or $NHCOCH_3$) in the 5 position of the hetero radical of investigated dyes causes either a slight hypsochromic shift of the absorption maximum or is practically without influence on the color. A noticeable deepening of the color is observed when a bromine atom is introduced in the 5 position. The entrance of a nitro group produces an even greater bathochromic effect. The presence of two electronegative groups in positions 1 and 5 of the investigated dyes leads to further considerable deepening of the color. The observed bathochromic shift is close to the sum of the shifts produced by the introduction of each of these groups separately.

In studying the absorption spectra of the dye – the unsubstituted derivative of oxindole – in solvents of different polarity it was established that in ethyl alcohol the electron shifts from the nitrogen of the diethylamino

TABLE 1

R'	R	Absorption maximum (in mμ)	Shift (in mμ)
H	H	487	—
H	CH_3	484	— 3
CH_3	CH_3	484	— 3
OH	CH_3	482	— 5
OCH_3	CH_3	486	— 1
$NHCOCH_3$	CH_3	487	0
$NHCOCH_3$	H	487	0
NO_2	H	524	+37
NO_2	CH_3	524	+37
Br	H	506	+19
Br	CH_3	502	+15
Br	C_2H_5	498	+11
Br	C_6H_5	518	+31
Br	$COCH_3$	530	+43

group to the carbonyl oxygen are comparatively small, obviously due to the reaction of the latter with the nitrogen of the hetero radical.

The introduction of a nitro group in the 5 position of the oxindole radical, attracting electrons, leads to a weakening of reaction between the hetero atoms and the carbonyl oxygen and in that way increases the electron shifts along the conjugation chain. Here the electron density distribution in the chromophore evidently becomes more uniform, which leads to a color deepening of the dye. The same effect is observed when a bromine atom is introduced in the 5 position of the hetero radical, where the main induction influence of the halogen atom appears.

The presence of an additional electronegative group in the 1 position weakens to an even greater degree the electron interactions between the hetero atom and the carbonyl oxygen, which facilitates even greater equalization of the electron density in the chromophore and in that way leads to a further deepening of color.

EXPERIMENTAL

Synthesis of Oxindole Derivatives

1,5-Dimethyloxindole. a) N-Chloroacetyl-N-methyl-p-toluidine. To a solution of 33 g of N-methyl-p-toluidine in 130 ml of benzene was added with shaking a solution of 17 g of chloroacetyl chloride in 60 ml of dry benzene. After several hours the obtained precipitate of methyltoluidine hydrochloride was filtered and washed with benzene. The benzene solutions were combined, washed with 30% acetic aicd, then with water, and dried over sodium sulfate. The benzene was distilled under reduced pressure. The residue was vacuum-distilled at 10 mm. Almost all of the substance distilled at 185°. Yield: 78%, pinkish oil; crystallized on standing; m.p. 55°.

Found %: N 7.47. $C_{10}H_{12}ONCl$. Calculated %: N 7.47.

b) A mixture of 2.5 g of N-chloroacetyl-N-methyl-p-toluidine and 2.5 g of aluminum chloride in a flask fitted with an air condenser and calcium chloride tube was heated for 30 minutes at 145° and then another 2 hours at 160°. The melt was poured on a mixture of 20 g of ice and 3 ml of 10% hydrochloric acid. The resulting oil was extracted with ether, the extract dried over sodium sulfate, the ether distilled off, and the residue vacuum-distilled. A yellowish oil distilled at 148-150° (10 mm), which on long standing or when seeded with the pure product completely crystallized. After two recrystallizations from water the 1,5-dimethyloxindole was obtained as colorless leaflets with m.p. 92°. Yield 1.02 g (47%). Difficultly soluble in cold water, more readily soluble in hot water, and very soluble in alcohol and ether.

Found %: N 8.78, 8.79. $C_{10}H_{11}ON$. Calculated %: N 8.69.

We synthesized 1-methyl-5-hydroxyoxindole [2] from N-acetyl-p-anisidine, via N-methyl-p-anisidine and N-methyl-N-chloroacetyl-p-anisidine [2]. Yield 83%. Grayish leaflets with m.p. 185-186° (186° [2]).

1-Methyl-5-methoxyoxindole [2] was obtained by treating an alkaline solution of 1-methyl-5-hydroxyoxindole with dimethyl sulfate. Yield 80%. Colorless crystals with m.p. 92° (92 °[2]).

5-Nitrooxindole [3-5]. To a solution of 4 g of oxindole in 30 ml of sulfuric acid at 0-2° was added 3.3 g of potassium nitrate. The mixture was kept at this temperature for 30 minutes and then poured on ice. The precipitate was filtered, washed with water, and dried in a desiccator.. Weight 4.8 g. Orange-brown powder with m.p. ~ 130°. The product was recrystallized from water with the addition of charcoal (weight 2.75 g, m.p. 200-205°), then from ethyl alcohol (weight 1.5 g, m.p. 218-220°), and finally from 50% acetic acid. Yield 0.75 g (15%). M.p. 233-234°. Further purification failed to change the melting point (literature: m.p. 236° [4] and 240-241° [3], 175° [5]).

1-Methyl-5-nitrooxindole [2] was obtained in a similar manner from 5-nitrooxindole. It was purified by two recrystallizations from benzene. Yield 60%. M.p. 194-195° (196° [2]).

5-Acetaminooxindole. 5-Aminooxindole was obtained by the reduction of 5-nitrooxindole with stannous chloride in alcohol-aqueous hydrochloric acid medium. The use of metallic tin for the reduction gave us x-chloro-5-aminooxindole as the main reaction product.

a) Reduction of 5-Nitrooxindole with Stannous Chloride. A suspension of 5 g of 5-nitrooxindole in 100 ml of ethyl alcohol was added in 10 minutes at 50° to a solution of 35 g of stannous chloride in 35 ml of hydrochloric acid and 35 ml of alcohol. The mixture was boiled under reflux for 3 hours; here the precipitate dissolved and the yellow solution became nearly colorless. After standing for 12 hours the cooled solution gave a light-yellow precipitate, which was filtered, washed with water, and again dissolved in water. Tin sulfide was precipitated when hydrogen sulfide was passed through the solution. The tin sulfide was filtered and washed with hot water. The filtrate and wash waters were evaporated to dryness. Here we obtained 3 g (58%) of 5-aminooxindole hydrochloride as a yellow-gray powder. A highly contaminated product was obtained from the acid filtrate after removing the binary salt of the amine with stannic chloride.

Treatment of an aqueous solution of 5-aminooxindole hydrochloride with ammonia gave 5-aminooxindole. After recrystallization from benzene with the addition of carbon and zinc dust, m.p. 213-214°.

Found %: N 18.97. $C_8H_8ON_2$. Calculated %: N 18.91.

b) Reduction of 5-Nitrooxindole with Metallic Tin. A mixture of 3.6 g of 5-nitrooxindole, 18 ml of hydrochloric acid (d 1.17) and 8 g of spongy tin was heated for 3 hours on the boiling water bath with stirring. Then 5 ml of ethyl alcohol was added and the heating continued another hour on the boiling water bath and then 1.5 hours at the boil; here the precipitate of the 5-nitro product dissolved completely. The unreacted tin was filtered and washed with hot water. The wash water was added to the main solution, which was then treated as indicated above (see "a"). After precipitating the tin sulfide the filtrate was evaporated to incipient crystallization. After cooling, the precipitate of the amine salt was filtered, washed with water, and dried in a desiccator. Weight 1.2 g. Further evaporation of the solution gave a thick dark-brown mass, from which individual products could not be isolated. The obtained hydrochloride was dissolved in water, and treatment of the solution with ammonia gave the free base as a precipitate, which was filtered, washed with water, and dried in a desiccator. Weight 0.8 g. M. p. ~ 220°. The base was recrystallized twice from benzene with the addition of carbon and zinc dust. Light, slightly grayish leaflets with m.p. 225°.

Found %: N 15.24, 15.47; Cl 19.30. $C_8H_7ON_2Cl$. Calculated %: N 15.35; Cl 19.42.

The acetylation of 5-amino-x-chlorooxindole (similar to the preparation of 5-acetaminooxindole) gave colorless crystals (from alcohol), m.p. 266°.

Found %: N 12.42, 12.04; Cl 15.60. $C_{10}H_9O_2N_2Cl$. Calculated %: N 12.03; Cl 15.79.

5-Acetaminooxindole. A solution of 2 g of 5-aminooxindole hydrochloride in 20 ml of water was treated with 3.5 g of acetic anhydride and 0.88 g of sodium acetate. The mixture was shaken vigorously for 5 minutes. The precipitate was filtered, washed with water, and dried in a desiccator. M.p. 270°. Yield 72%. Recrystallization from benzene gave fine, almost colorless crystals with m.p. 275°.

Found %: N 14.60. $C_{10}H_{10}O_2N_2$. Calculated %: N 14.73.

1-Methyl-5-acetaminooxindole was synthesized from 1-methyl-5-nitrooxindole through the hydrochloride of 1-methyl-5-aminooxindole, similar to the preparation of 5-acetaminooxindole. Colorless leaflets with m.p. 240-241°. Very difficultly soluble in water and quite soluble in ethyl alcohol and hot benzene.

Found %: N 13.58. $C_{11}H_{12}O_2N_2$. Calculated %: N 13.72.

5-Bromooxindole was obtained by the bomination of oxindole in water solution containing potassium bromide [6]. The product was recrystallized twice from ethyl alcohol with the addition of carbon. Yield 50%. M.p. 219-220° (220-221° [6]).

5-Bromo-1-methyloxindole. Obtained by shaking a solution of 1-methyloxindole in carbon tetrachloride with bromine water [7]. Yield 84%. Purified by recrystallization from gasoline (b. p. 90-115°). M. p. 132-133° (133° [7]).

TABLE 2

Value in formula (I)		Amount			length of heating (in hours)	Purification method (recrystd.– recrystallized, chrom.– chromatographed)	Yield of dye (total/purified substance)	External appearance	Melting point	Analysis		
										found N (in %)	calculated	
R'	R	of oxindole derivative (in g)	of p-nitrosodiethylaniline (in g)	of alcohol (in ml)							formula	N %
CH_3	CH_3	0.48	0.54	9	1	Recrystd. twice from C_2H_5OH	55/–	Brown red glistening plates	188° (decomp)	13.20 13.23	$C_{20}H_{23}ON_3$	13.08
OH	CH_3	0.11	0.12	2	1	Recrystd. twice from C_2H_5OH	–/38	Fine dark-brown needles	203–204	12.87 12.81	$C_{19}H_{21}O_2N_3$	13.00
CH_3O	CH_3	0.35	0.35	6	1	Recrystd. twice from C_2H_5OH	60/–	Dark-brown glistening needles	160	12.32	$C_{20}H_{23}O_2N_3$	12.46
NO_2	H	0.72	0.72	10	3	Chrom. in $CHCl_3 + C_6H_6$, eluted with C_6H_6 (yellow solution), then with $CHCl_3$ (blue and red solutions), separates from the red solution. Chrom. from C_6H_6	60/30	Fine dark-brown prisms	219 (decomp)	16.55 16.52	$C_{18}H_{18}O_3N_4$	16.57
NO_2	CH_3	0.77	0.72	13.5	1	Recrystd. twice from C_6H_6, chrom. in $CHCl_3$, recrystd. from C_6H_6	57/–	Fine brown needles	195 (decomp)	15.93	$C_{19}H_{20}O_3N_4$	15.91
$NHCOCH_3$	H	0.57	0.53	9	1	Recrystd. 3 times from C_2H_5OH	70/–	Violet-red pyramidal crystals	218 (decomp)	16.06	$C_{20}H_{22}O_2N_4$	15.99
$NHCOCH_3$	CH_3	0.20	0.18	2.5	1	Recrystd. from C_2H_5OH	–/33	Fine orange-red needles	201-202 (decomp)	15.17	$C_{21}H_{24}O_2N_4$	15.32
Br	H	1.06	0.89	10	0.5	Chrom. in $CHCl_3 + C_6H_6$, eluted with C_6H_6, recrystd. from C_2H_5OH	64/26	Very fine lustrous red leaflets	198 (decomp)	11.15 11.15	$C_{18}H_{18}ON_3Br$	11.26
Br	CH_3	0.68	0.53	10	1	Chrom. in $CHCl_3 + C_6H_6$ and recrystd. from C_2H_5OH	68/35	Very fine red-brown needles	195	10.85	$C_{19}H_{20}ON_3Br$	10.88
Br	C_2H_5	0.72	0.53	6	1	Recrystd. from C_2H_5OH, chrom. in C_6H_6, recrystd. from C_2H_5OH	63/20	Fine red plates or prisms	165 (decomp)	10.65 10.52	$C_{20}H_{22}ON_3Br$	10.52
Br	C_6H_5	0.87	0.53	6	1	Recrystd. 3 times from C_2H_5OH	60/17	Fine dark-red needles or prisms	173 (decomp)	9.57 9.67	$C_{24}H_{22}ON_3Br$	9.35
Br	$COCH_3$	0.51	0.36	7	3	Chrom. in $CHCl_3 + C_6H_6$, eluted with C_6H_6, recrystd. from C_2H_5OH	63/26	Fine brown plates	195 (decomp)	9.97 10.00	$C_{20}H_{20}O_2N_3Br$	10.14

5-Bromo-1-ethyloxindole. Synthesized in the same manner as the N-methyl derivative. Yield 71%. M.p. 107-108° (108° [7]).

5-Bromo-1-phenyloxindole. A solution of 4.2 g of 1-phenyloxindole in 80 ml of carbon tetrachloride was shaken in a separatory funnel with 3.4 g of bromine in 180 ml of water until the bromine color disappeared. On standing a yellowish precipitate separated from the mixture, which was filtered, washed with water, and dried at 50-60°. Weight 3.6 g. M.p. 149-151°. The carbon tetrachloride layer was separated and evaporated in vacuo to 1/3 volume. The resulting precipitate was filtered, washed with 10 ml of hot alcohol, recrystallized from alcohol (weight 0.6 g, m.p. 150-152°), and added to the first precipitate. Total yield 4.2 g (74%). The obtained 5-bromo-1-phenyloxindole was recrystallized from ethyl alcohol. Weight 2.7 g (47%). M.p. 162-163° (162° [7]).

5-Bromo-1-acetyloxindole. A mixture of 2.1 g of 5-bromooxindole and 3 g of acetic anhydride was heated in a flask under reflux for 7 hours at 135-145° and allowed to stand to the next day. The obtained crystals were filtered, washed with alcohol, and dried. Yield 1.5 g. Recrystallization from ethyl alcohol gave colorless crystals with m.p. 132-133°.

Found %: C 47.10; H 3.30. $C_{10}H_8O_2NBr$. Calculated %: C 47.20; H 3.13.

Preparation of p-Diethylaminoanils of (3)-Substituted Isatins

The dyes were obtained by boiling an alcohol solution of equimolar amounts of the oxindole derivative and p-nitrosodiethylaniline in the presence of piperidine traces. After cooling, the dye precipitate was filtered and washed with alcohol. For Purification some of the dyes were recrystallized from ethyl alcohol. In a number of cases they were chromatographed on aluminum oxide in a mixture of chloroform and benzene (1:1). The dyes were eluted from the aluminum oxide with the same mixture or with benzene alone. The solution obtained after chromatographing was evaporated in vacuo to dryness, and the dye was further recrystallized from ethyl alcohol. The conditions used to prepare the dyes, the method of purification their properties and the analysis results are all tabulated in Table 2.

SUMMARY

1. A number of azomethine dyes were synthesized, being oxindole derivatives and specifically the p-diethylaminoanils of (3)-substituted isatins, having different substituting groups in the 5 or in the 5 and 1 positions of the hetero radical; absorption spectra in the visible region of their alcohol solutions were studied.

2. It was established that the introduction of weakly electropositive groups (CH_3,OH,OCH_3,$NHCOCH_3$) in 5 position of hetero radical in these dyes either causes slight hypsochromic shift or is without affect on the color. Noticeable deepening of the color is observed when either a nitro group or a bromine atom is present in this position, which is made even deeper by introducing a second electronegative group on the nitrogen atom of the hetero radical.

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Moscow Institute
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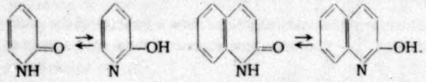
THE TAUTOMERISM OF α-PYRIDONE AND CARBOSTYRIL

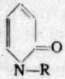
M. I. Kabachnik, S. T. Ioffe and Yu. N. Sheinker

A classic and well studied example of lactim-lactam tautomerism is the tautomerism of α-pyridone and of carbostyril.

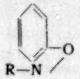


Even at the end of the last century Decker [1] depicted the structure of alkylpyridones by formula (I). The absence of characteristic reactions for the carbonyl group and the inability shown by alkyl halides to add to trivalent nitrogen motivated Fischer [2] to propose structure (II), which however failed to withstand criticism, due to the presence of a pentacovalent nitrogen. Later Auwers [3] and Arndt [4] proposed the bipolar structure (III) without explaining the inability of N-alkylpyridones to add alkyl halides. By analogy with the structure of substituted α-piperidones, Gautier [5] compared the carbonyl group of pyridone to the carbonyl group of amides.

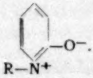
(I)



(II)



(III)



The pyridone nucleus is capable of both aromatic substitution reactions (halogenation [5], nitration [6]) and of catalytic hydrogenation under conditions that are typical for substances with conjugated bonds. Also known is a large number of reactions, characteristic for both the lactim (hydroxypyridine) and lactam (pyridone) forms. Pyridones show, although to considerably less degree, reaction with ferric chloride, a reaction typical for phenols, and also the ability to couple with diazonium salts [7]. The reaction of either phosphorus pentachloride or phosphorus oxychloride with pyridone and carbostyril leads to α-chloro derivatives of pyridine and quinoline. The alkylation of pyridone in alkaline medium with either methyl iodide or dimethyl sulfate gives mainly N-methylpyridone [8], whereas the treatment of pyridone in neutral solution with diazomethane yields 2-methoxypyridine as the sole reaction product [9]. Ketone reactions for both pyridone and carbostyril are absent. In their properties these substances resemble rather the N-substituted amides. Many authors have studied the dual reactivity shown by metal derivatives of α-hydroxypyridine and α-hydroxyquinoline [10] in alkylation reactions, leading to the formation of both O- and N-substituted derivatives. The close similarity of the ultraviolet spectra for hydroxypyridine and N-methylpyridone indicates the pyridone form of 2-hydroxypyridine [11], whereas the absorption spectrum of 2-ethoxypyridine in neutral solution is quite different from the spectrum of pyridone. The lactam form for carbostyril was ascertained by a similar spectral method [12].

When infrared absorption spectra were used it was shown that both in the crystalline state and in solutions the lactam form is characteristic for the α- and γ-hydroxypyridines [13], carbostyril and a number of other α- and γ-hydroxy derivatives of the heterocyclic series. Together with this it should be mentioned that the sensitivity of the spectral methods used in these studies was insufficient to reveal small amounts of the hydroxy forms (lactims).

In addition, the IR-spectral method is not suitable for showing OH groups in substances dissolved in hydroxyl-containing solvents. Since the tautomeric lactim-lactam equilibrium belongs to the class of rapidly established equilibria, then an analytical determination of either the lactim form or of the position of the equilibrium did not seem possible, due to the too rapid mutual transformation rate shown by the forms, exceeding the rate of the used analytical reactions. Consequently, we used the potentiometric method in an attempt to determine the position of tautomeric equilibrium. This method, developed by two of us on the example of a slowly established keto-enol equilibrium [14], was also used successfully to determine the position of the rapidly established equilibrium for the tautomeric dialkyl monothiophosphates [15]. As standards for the potentiometric measurements we took, on the one hand, N-alkyl derivatives of pyridone and carbostyril, and on the other, 2-alkoxy derivatives of pyridine and quinoline. The measurements were made in water and in 80% (by volume) alcohol solutions, partially neutralized with 0.05N HCl, at a concentration of 0.005N and a temperature of 20°, using a glass electrode and a lamp potentiometer of the LP-5 type (the measurement accuracy was 0.04 of a pH unit). Calculation was based on a simplified form of the equation used to determine the ionization constants of bases, namely [16]:

$K_b = \frac{([Cl^-]-[H^+])}{M-([Cl^-]-[H^+])} \cdot \frac{K_W}{[H^+]}$, where M is the concentration and K_W is the ionization constant of water. The measurement results are summarized in the table.

In alcohol the 2-alkoxypyridines and quinolines show a basicity of the order of 10^{-12}, and in water appear as somewhat stronger bases (10^{-11}). The ionization exponents show good agreement with the Brönsted equation: a linear relationship with tan α = 1 (Fig. 1, points 4,5 and 6). As was to be expected, the N-alkyl derivatives of pyridone and carbostyril proved to be extremely weak bases (the ionization constants in water are of the order of 10^{-13}, and in alcohol of the order of 10^{-12}). Pyridone, carbostyril and 4,6-dimethyl-2-pyridone in their basic properties proved to be very close to the N-alkyl derivatives and the points, corresponding to their ionization exponents (Fig. 1, points 7,8 and 9), lie with slight scattering near the points of the N-alkyl derivatives. The ionization exponents of both the tautomeric substances and the N-alkyl derivatives also satisfy a linear relationship with tan α = 1 (Fig. 1, points 1,2,3,7,8 and 9).

Point Nos. in Fig. 1	Substance	pK_b in water*	pK_b in 80% alcohol
1	N-Methylpyridone	12.16	11.27
2	N-Ethylpyridone	12.37	11.42
3	N-Methylquinoline	12.38	11.44
4	2-Methoxypyridine	10.57	11.10
5	2-Methoxyquinoline	11.19	11.75
6	2-Ethoxyquinoline	10.96	11.58
7	α-Pyridone	12.17	11.34
8	Carbostyril	12.52	11.56
9	4,6-Dimethyl-2-pyridone	12.26	11.45

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* Due to the limited solubility of some of the substances, all of the measurements were made in 7% alcohol.

This can be explained only by the fact that the tautomeric equilibrium of both pyridone and carbostyril is shifted essentially in the direction of the lactam form. From an evaluation of the accuracy of the pH measurements made in the experimental portion of this work and the scattering of the points under parallel measurements for the same substance it can be concluded that under our conditions the potentiometric method did not permit obtaining an accuracy greater than that needed to reveal 0.5-1% of the tautomeric lactim form. As a result, the data obtained by this method are found to be in full agreement with the data of other methods and again offer evidence in support of the essential predominance of the lactam form in tautomeric equilibrium. However, we failed in our attempt to quantitatively ascertain the equilibrium position. In addition, the closeness of the K_b values for all of the studied lactams and lactims permits assuming that here the equilibrium cannot be shifted in very high degree (as, for example, for kynurin, where the difference in the ionization constants of N-methyl-4-quinolone and 4-hydroxyquinoline is about 4 digits [17]). In any case, there still lacks a reliable base for the conclusion that tautomeric lactim-lactam equilibrium is shifted to the lactam side to such extent as to prevent the possibility of forming two series of derivatives as the result of each of the tautomeric forms showing reaction (reaction progressing without transfer of reaction center).

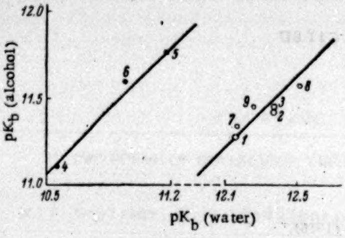

Fig. 1

Desiring to evaluate the influence of ortho and para orienting substituents in various positions of the pyridone ring on the equilibrium position, we prepared, in addition to the above-mentioned 4,6-dimethylpyridone, also the 5-iodo-, 5-bromo- and 3,5-dibromopyridones, and the 5-bromo-2-methoxypyridine.* However, it proved impossible to measure the ionization constants of the halo derivatives due to their extremely weak basicity; consequently, all of these compounds were studied by means of their infrared spectra.

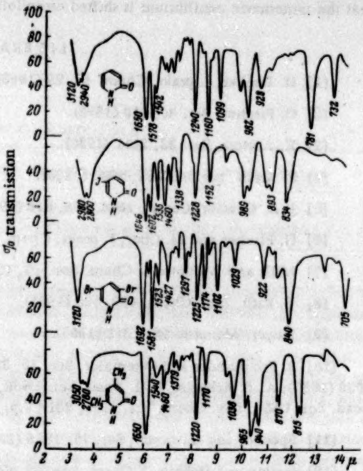

Fig. 2

The IR spectra of 5-bromo-, 5-iodo-, 3,5-dibromo- and 4,6-dimethyl-2-pyridone, both in the crystalline state and in solution (in alcohol), all show an intense absorption band in the 1650 cm^{-1} region, belonging, as had already been discussed [13], to the carbonyl group C=O in lactams. To a large degree the spectra of these compounds resemble the spectrum of pyridone itself (Fig. 2) and differ noticeably from the spectra of either 2-methoxy-5-bromopyridine or 2-ethoxypyridine (which, incidentally, closely resemble each other, Fig. 3). Of interest is the fact that the carbonyl band in 3,5-dibromopyridone shows a very high frequency (1692 cm^{-1}), which apparently is associated here with the absence of intermolecular hydrogen bonds – C=O ⋯ H–N due to steric hindrance (the adjacency of the bromine atom to the C=O group). It is possible that a certain lack of electron density distribution from the carbonyl oxygen to the bromine also plays a definite role here.

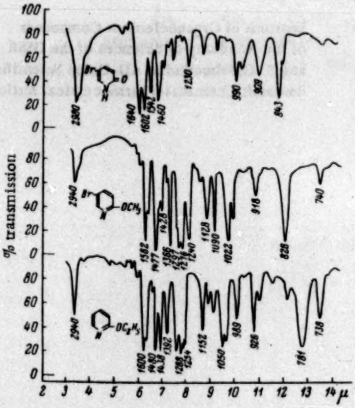

Fig. 3

As a result, there is no evidence in support of a noticeable shift in tautomeric equilibrium when ortho and para orienting substituents are introduced in the pyridone ring – halogens in the 3 and 5 positions or methyl groups in the 4 and 6 positions.

SUMMARY

1. Based on pH measurement of partially neutralized solutions the ionization constants of the following compounds in water and in 80% alcohol were calculated: pyridone, carbostyril, N-methylpyridone, N-ethylpyridone, N-methylquinoline, 4,6-dimethylpyridone, 2-methoxyquinoline, 2-ethoxyquinoline and 2-methoxypyridine.

2. The infrared spectra of the indicated compounds were taken, and also those of the 5-iodo-, 5-bromo-

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* L. A. Bogdanova assisted in the experimental part.

and 3,5-dibromo- pyridones, and of 5-bromo-2-methoxypyridine.

3. With the aid of the potentiometric method and on the basis of infrared spectra it was concluded that the tautomeric equilibrium is shifted essentially to the side of the lactam form.

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Institute of Organoelement Compounds
of the Academy of Sciences of the USSR
and S. Ordzhonikidze All-Union Scientific-
Research Chemical-Pharmaceutical Institute

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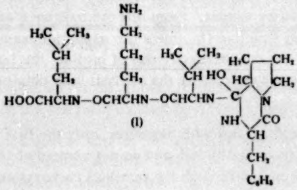
THE STRUCTURE OF GRAMICIDIN S

V. TWO FORMS OF GRAMICIDIN, THEIR MUTUAL TRANSFORMATIONS AND STRUCTURE

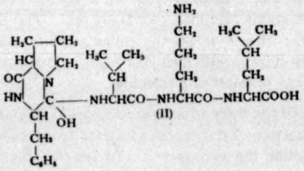
N. I. Gavrilov, N. A. Poddubnaya, L. N. Akimova and E. M. Grigoryeva

To establish the structure of gramicidin S we [1-5] and a number of other investigators [6-10] used various methods, including destruction of the molecule, electroreduction, partial hydrolysis, and also spectrophotometry of the copper biuret complexes. The utilization of these methods made it possible to establish the architectural details of gramicidin and show the absence of a cyclopolypeptide structure in this antibiotic. As a result, the presence of both cyclic and peptide types of bonds in the gramicidin S structure can be considered to be without doubt. Some of them, i.e. the cyclic types, are represented by phenylalanyl-prolyl-diketopiperazine, while the other types are found in the side peptide portion, containing valine, ornithine and leucine. The presence of the phenylalanyl-prolyldiketopiperazine was established by electroreduction of the gramicidin and its isolation by acid hydrolysis [5], while the tripeptide structure of the peptide portion of gramicidin follows from the analysis data of its copper biuret complexes [3] (spectrophotometry, "copper numbers"). By studying the biuret reaction of gramicidin under various conditions it proved possible to show the character of the bonds between the individual structural elements and to establish the dimeric character of gramicidin S.

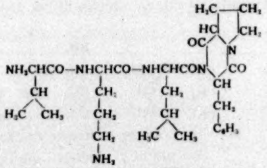
What are our theories relative to the bond forms of the individual structures in the gramicidin monomer with its subsequent transition into the gramicidin dimer? Below are shown the possible combinations with each other of the component parts of gramicidin, the diketopiperazine and the tripeptide (the amino acid sequence given by Synge [7] was used).



(I)



(II)



(III)

The presence of phenylalanyl-prolyl-valine among the decomposition products of gramicidin can be explained by the hydrolysis of structure (I). However, the formation of leucylphenylalanine in the gramicidin hydrolyzate cannot be explained with this structure.

The hydrolysis of gramicidin in accord with structure (II) could yield two tripeptides: prolyl-phenylalanyl-valine or valyl-phenylalanyl-proline. Neither of these tripeptides was isolated in the hydrolysis of gramicidin. As a result, it is impossible to explain the formation of either phenylalanyl-prolyl-valine or leucyl-phenylalanine with this structure.

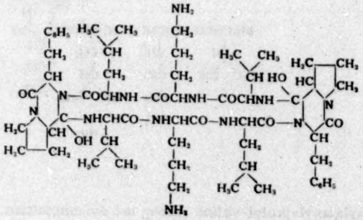
With structure (III) it is impossible to explain the finding of phenylalanyl-prolyl-valine in the gramicidin hydrolyzate. Therefore all of the found dipeptides show good agreement with such a structure. The formation of leucyl-phenylalanine can also be explained with this structure.

In addition, according to structures (I) and (II) gramicidin should show a free carboxyl group, and according to (III) – a free amino group. With the exception of the ornithine amino group, it was established by analysis that both a free carboxyl and a free amino group are absent in the gramicidin S molecule. Since we represent gramicidin as a dimer, in which the mentioned monomer structures can show coupling between themselves, then the basic problem relative to the structure of gramicidin reduces to an examination of the bond between the phenylalanyl-prolyl-diketopiperazine and the tripeptide in the monomer

At the present time two forms of the diketopiperazine bond with amino acids and with peptides have been shown by synthesis – the amidine form and the N-aminoacyl. The extent to which the mentioned structures are real can be seen from a comparison of the hypothetical structures with the compounds isolated in the hydrolysis of gramicidin S. This comparison enables us to select the structure that is in fullest accord with experimental observation.

The following dipeptides were obtained in the hydrolysis of gramicidin S: valyl-ornithine, ornithyl-leucine, leucyl-phenylalanine and phenylalanyl-proline, which shows good agreement with the data for the decomposition of structure (III). In addition to the enumerated dipeptides, we also isolated the tripeptides – phenylalanyl-prolyl-valine and valyl-ornithyl-leucine – from the decomposition products of gramicidin. The first tripeptide is evidence that two of the amino acids in the gramicidin structure, namely proline and valine, should be linked with each other. Since such a tripeptide cannot be obtained when decomposition is in accord with structure (III), then it is natural to assume that the gramicidin molecule should also contain a grouping in which the proline carboxyl group is linked with the valine amino group. For this we will examine structures (I) and (II), in which union is realized through the valine amino group. In structure (II) the valine is linked with the carboxyl group of phenylalanine. This means that hydrolysis of such a structure can yield only prolyl-phenylalanyl-valine or valyl-phenylalanyl-proline, i.e. a tripeptide that has never been isolated by anyone. From this the existence of structural formula (II) for the gramicidin monomer is not real. This leaves structure (I), where the tripeptide bond with the diketopiperazine is realized through the amino group of valine and the carboxyl group of proline, the latter in turn showing lactam linkage with phenyl-alanine. This structure is supported by the analysis data obtained for the hydrolytic cleavage products of gramicidin.

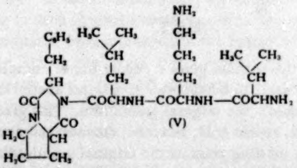
Of the three structural formulas examined for the gramicidin monomer, only the first and third agree with the structure of the peptides isolated in the hydrolysis of gramicidin and do not contradict experiment. Therefore, in gramicidin the two structures (I) and (III) should be united through the terminal carboxyl and amino groups of the monomers, and the resulting dimer should show two free δ-amino groups of ornithine, which is also found in accord with the data on the dinitro derivatives of gramicidin with respect to the terminal amino groups. Proceeding from structures (I) and (III), the total formula for the gramicidin dimer can be represented by structure (IV).



(IV)

Earlier it had been shown that gramicidin S forms two types of copper complexes with a maximum at 570 mμ for the "violet" and a maximum at 535 mμ for the "red". The "violet" copper complex, indicating the presence of a tripeptide chain in the gramicidin structure, on standing with copper in alkaline medium shows the ability of being transformed into the "red" complex. At the same time the regeneration of the "violet" complex from the "red" was observed on acidification. Without a doubt this transition of the copper biuret complex of gramicidin from an "incomplete violet" to a "complete red" complex is associated with some structural characteristics of the gramicidin, which we attempted to decipher.

For this purpose we prepared the "red" form of gramicidin, and by careful decomposition of its copper salt under slight acidification with hydrochloric acid we isolated gramicidin as the monomer. A study of the properties of this gramicidin revealed that it was different from the starting gramicidin, the difference reducing to the fact that its molecular weight was one half that of native gramicidin. Proceeding from the examined structures (I) and (III), the gramicidin monomer can show either terminal carboxyl or amino groups. In addition to these functional groups, such gramicidin monomers should also differ from each other in the forms of the diketopiperazine bonds with the tripeptide. In the first case the structure of the monomer with a terminal carboxyl group should contain the amidine bond, and in the second case – with a terminal amino group – the N-aminoacyl linkage. In the gramicidin regenerated from the "red" form it was the terminal amino group that was shown (by the Wilstatter method), which permitted assigning structure (V) to the gramicidin S monomer: *



(V)

At the same time the bond existing between these two monomers was deciphered, being accomplished through the free terminal amino groups of valine. This bond required the presence of two amidine groups in the gramicidin dimer structure.

A detailed study of the regeneration conditions for gramicidin revealed that the dimerization is possible only in 50 % alcohol in the presence of acid. In 96% alcohol in the presence of acid the amino groups do not aminate, as a result of which they are incapable of forming the amidine bond under these conditions, which is confirmed by the absence of dimerization in 96% alcohol. In contrast to dimerization, the monomerization, associated with decomposition of the dimer at the amidine bonds, proceeds only in alkaline medium, which is in good agreement with the instability shown by some amidines in alkaline solutions.

A structure analogous to that of the gramicidin monomer was found in the molecule of the ergot alkaloids [11]. In the main the structure of these alkaloids was studied by hydrolytic methods, such as: cleavage with either hydrazine or alkali, thermal decomposition, and in addition, reduction with lithium aluminum hydride. The reduction method proved especially fruitful, permitting not only the establishment of a diketopiperazine ring in the structure of the alkaloids, but also indicating the form of the bond between this ring and the peptide portion of the rest of the molecule. Thus, the isolation of substituted piperazine derivatives from the reduction products is evidence of the corresponding N-aminoacyl bond, which was also established by us for gramicidin.

EXPERIMENTAL

I. Regeneration of Gramicidin S From the Red Copper Complex. a) From 50% Alcohol Solution. Earlier it had been shown that gramicidin S in 50% alcohol forms with copper the "violet" copper complex with a maximum at 570-575 mμ. On standing for 3 days with $Cu(OH)_2$ this complex migrates into the "red" form** with a light-absorption maximum at 535 m μ [3]. When this complex was decomposed by acidification with concentrated hydrochloric acid a precipitate was obtained, which proved to be the original gramicidin with m.p. 278-280°.

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* A. B. Silaev [1] was the first to express a theory relative to the structure of the gramicidin monomer.

**The structural form of gramicidin S, corresponding to the copper complex with a red color, we tentatively designate as the "red form".

Yield 86%. The chromatogram of the regenerated gramicidin (Fig. 1) in butanol-water-glacial acetic acid medium in the ratio 4:5:1, when compared with that of the original gramicidin (m.p. 278°), showed the similarity of the two. The mixed melting point with the original gramicidin failed to be depressed. The Rf of the regenerated and original gramicidin is the same and equal to 0.85.

b) From 96% Ethyl Alcohol. To obtain the "red" form we prepared a solution of the copper biuret complex of gramicidin S in 96% alcohol. After 7.5 days this solution with a light-absorption maximum for the copper complex of 535 m μ was made slightly acid with alcoholic hydrochloric acid solution. The regenerated gramicidin was extracted with chloroform, separated from the solution, and the chloroform was vacuum-distilled without heating. The gramicidin yield was 96 %, m.p. 278-281°. M. p. of the original gramicidin was 278-281°.

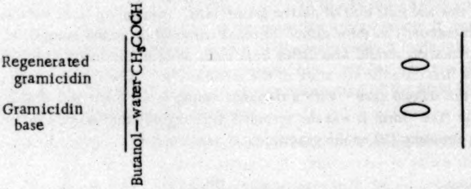

Fig. 1

The gramicidin obtained in this manner gives a copper biuret complex with a light-absorption maximum at 535 mμ. Its chromatogram on paper, in butanol-water-glacial acetic acid medium (4:5:1), gives the same distribution coefficient as the standard – the original gramicidin. This gramicidin is readily soluble in ethyl, methyl, butyl and isoamyl alcohols, acetic acid, benzene, dioxane and acetone. The melting point of the gramicidin monomer coincides with the melting point of the original gramicidin S (regeneration occurs during melting). The biological activity of the gramicidin monomer corresponds to that of the original gramicidin.* Repeated checking of the electrochromatogram revealed that the "red" form of gramicidin moves at a slower rate to the cathode side than does the original gramicidin. The ionophoresis experiments were run in acetic acid at 110 V and a potential gradient of 2 V/cm² (Fig. 2). The determination of amino nitrogen in the original gramicidin and in its "red" form by the Wilstatter method showed the presence in the latter, in contrast to the original, of an additional amino group (besides the δ-amino group of ornithine).

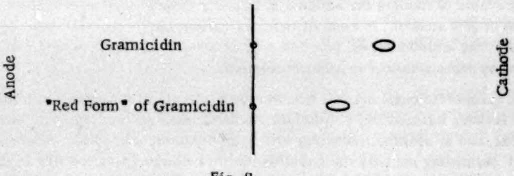

Fig. 2

"Red Form" of Gramicidin

Found %: NH_2 4.68. $C_{30}H_{48}O_5N_6Cl_2$.
Calculated %: NH_2 4.60.

Original Gramicidin

Found %: NH_2 2.6. $C_{60}H_{94}O_{10}N_{12}Cl_2$.
Calculated %: NH_2 2.3.

The molecular weight of the "red form" of gramicidin S, determined (see Table) from the equation of solution densities (in alcohol and in acetone) [12], is equal to 572. The molecular weight of the gramicidin monomer, determined by the Rast method in camphor, is equal to 1160. In view of the fact that the melt * of gramicidin with camphor gave a copper complex with a maximum at 560 m μ it is most probable to assume that dimerization of the gramicidin occurs when its molecular weight is determined by the Rast method.

Molecular Weight Determination by the Barger Method [12]. 15.6 mg of the "red form" of gramicidin S was dissolved in 10 ml of 96 % alcohol and 0.1 ml of this solution was placed in a capillary with d = 2 mm and l = 20 cm.

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* We wish to thank A. B. Silaev for determining the activity of this and other preparations.

** 0.9 mg of the "red form" of gramicidin S was fused with 20 mg of camphor at 210-220°. The copper complex was prepared from the melt in the usual manner.

In the same capillary, from the other end, was placed 0.1 ml of a solution of gramicidin base (15.7 mg in 10 ml of 96% alcohol). The capillary, sealed at both ends, was glued to a glass plate with the (null point) hairline nearer the studied solution, and the change in the volume of the drops of the studied solution was observed under the microscope, using a micrometer scale. After 2-3 days the solution concentrations became equalized and the dimensions of the columns of liquid in the capillary assumed a constant value. The molecular weight was calculated from the formula:

$$M = \frac{p_1 P_2 M_2}{p_2 P_1},$$

where p_1 is the weight of the "red" gramicidin, p_2 is the weight of the "violet" gramicidin, and P_1 and P_2 are respectively the weight of the solvent, determined by the dimensions of the column of liquid in the capillary. The experimental results for determination of the molecular weight by the Rast and Barger method are summarized in the Table.

II. Regeneration of Desaminated Gramicidin S. As we had published earlier [13], gramicidin S that had been desaminated at the δ-NH_2 group of ornithine is also capable, after forming a primary copper complex with a light-absorption maximum at wavelength 540 mμ, of transformation with time (70 hours) into a new form with a light-absorption maximum at 510 mμ. In the isolation of the desaminated gramicidin with maximum at 510 mμ from a solution of its copper complex in 96% alcohol a monomer with the same maximum was isolated. When the desaminated gramicidin was regenerated from a solution of the copper complex in 50% alcohol we failed to obtain the monomer. Regeneration in 50% alcohol leads to the original gramicidin with a light-absorption maximum at wavelength 540 mμ. As a result, the gramicidin transformations studied by us and also repeated with the desaminated form, are a function of the whole structure.

TABLE

Determination of the Molecular Weight for Gramicidin and its "Red" Form by the Rast Barger Methods

Method	Weight of studied compound (in mg)		Solvent	Weight of camphor (in mg)	Melting point of the melt	Comparative values of the colums of liquid in the capillary (in cm)		Molecular weight
	gramicidin S	"red" form of gramicidin S				gramicidin S (P_1)	"red" form of gramicidin S (P_2)	
Rast	9.0	—	Camphor	90.0	173.0°	—	—	1160
	—	9.0	"	90.0	172.9	—	—	1160
Barger	31.4	15.6	96% alcohol	—	—	5.0	5.0	578.9
	25.5	15.0	"	—	—	4.6	5.4	571.0
	15.7	15.6	"	—	—	6.7	3.3	567.6
	15.8	15.4	Absolute acetone	—	—	5.1	2.7	598.4
	31.4	7.85	"	—	—	3.4	6.6	561.6
	30.0	25.0	"	—	—	6.3	3.7	567.7
	7.3	8.4	Chloroform	—	—	7.1	2.9	545.19

SUMMARY

1. Slight acidification permits isolating from the copper biuret complexes of gramicidin S the following:

a) in the case of 96% alcohol the monomeric form of the gramicidin with a light-absorption maximum at 535 mμ ("red" form);

b) in the case of 50% alcohol the dimeric form is regenerated with a light-absorption maximum at 570 mμ ("violet" form);

c) the "red" form of gramicidin has two free amino groups, determined by the Wilstatter method.

2. The desaminated gramicidin behaves in the same manner as gramicidin in the formation of the copper complex. Its monomeric form shows a light-absorption maximum at wavelength 510 mμ, and the dimeric form at wavelength 540 mμ.

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*T.p. = C. B. Translation pagination.

ISOLATION OF A NEW ANTIBIOTIC [illegible]ONGISPORINE AND STUDY OF ITS CHEMICAL NATURE

G. P. Menshikov and M. M. Rubinshtein*

After N. A. Krasilnikov [1] had established the antibiotic activity of the culture liquor isolated by him from the strain No. 108 Actinomyces longisporus, it seemed of considerable interest to obtain the pure active principle for the purpose of studying its chemotherapeutical action and elucidating its chemical nature. The present study deals only with the chemical aspects of the problem, i.e., with the isolation of the pure antibiotic, which we have named longisporine, and a study of its chemical nature. It should be mentioned that longisporine proved to be very active in vitro against the tubercle bacillus, but its great toxicity (produces hemolysis) does not permit its use as a curative.

The pure antibiotic, the isolation and purification of which will be detailed in Experimental section, crystallizes from either anhydrous alcohol or petroleum ether as large snow-white prisms, melting at 99-101°, readily soluble in chloroform, alcohol and petroleum ether, and practically insoluble in water; it shows weak dextro rotation: $[\alpha]_D + 2.62°$ (c = 5; chloroform). The results of numerous elementary analyses of various longisporine specimens with m.p. 99-101° showed only very slight differences. Thus, for example, the carbon content varied from 66.23 to 66.65%, and the hydrogen from 8.86 to 9.12%. Nitrogen, sulfur and phosphorus were not detected in the substance. The molecular weight of the antibiotic was determined both cryoscopically (in benzene) and by the Rast method. All of the these determinations gave values that were exceedingly close to 650. These analytical data show good agreement with the formula $C_{36}H_{58}O_{10}$, for which the calculated %: C 66.42; H 9.00 and M 650.5.

Despite its content of 10 oxygen atoms, longisporine is a completely neutral substance, failing to dissolve in either alkalies or acids. Determination of its active hydrogen content by the Tserevitinov method also gave a negative result.

Some interesting data, throwing light on the chemical nature of longisporine, were obtained when its hydrolytic decomposition was studied. It proved that longisporine is capable of saponification, but at a considerably slower rate than the glycerides. If, as is known, for the latter, 1 hour of heating is sufficient to give the desired ester number, then for longisporine a considerably longer time is required, as can be seen from the table:

Time of heating (in hours)	Ester number
1	62
2	113
8	248

It can also be seen from this table that 1 longisporine molecule has 3 ester groups, since for a molecular weight of 650 the ester number should be equal to 258, which differs but slightly from the found ester number – 248. From this the question naturally arises: isn't the antibiotic isolated by us a glyceride, containing still unknown acid? True, the indicated postulation was refuted by the great stability shown by longisporine to alkalies, but this fact could not be considered decisive, and in this connection a study was made of the the hydrolysis products of the antibiotic; here a special attempt was made to find glycerin. It proved that even the saponification of 3 g of the substance, where about 0.4 g of glycerin should have been obtained, failed to show the presence of the latter.

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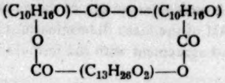
* Deceased.

From the hydrolysis products we were able to isolate in pure form only a crystalline acid, which after recrystallization from a mixture of equal volumes of benzene and petroleum ether was obtained as large colorless prisms with m.p. 64-65°. The elementary analyses, equivalent weight, found by acidimetric titration, and also the molecular weight, determined by the Rast method, gave for this acid the empirical formula $C_{11}H_{18}O_4$. The active hydrogen determination by the Tserevitinov method revealed that it contained 2 active hydrogen atoms. From this it must be concluded that the acid from longisporine is a hydroxy acid and its formula can be depicted as follows: $C_{10}H_{16}O(OH) \cdot COOH$. From this formula it can be seen that two of the oxygen atoms of the acid are bound in the carboxyl and one in the hydroxyl group. As regards the fourth oxygen, then in all probability it is bound as an ether linkage. This is indicated by the inability of the hydroxy acid to react with phenylhydrazine and with semicarbazide. The yield of acid from the saponification of longisporine had great value for understanding the chemical nature of the latter. It was found that 3 g of the antibiotic yields 1.2 g of the pure hydroxy acid. From this it follows that the longisporine molecule contains 2 radicals of this hydroxy acid, as otherwise its theoretical yield would be a total of only 0.99 g.

In the light of the discussed experimental data a number of conclusions can be made relative to the chemical nature of longisporine. As had already been mentioned, the latter has the composition $C_{36}H_{58}O_{10}$ and contains 3 ester groups. Consequently, its saponification should result in the absorption of 3 molecules of water and the formation of 3 acids, having a total of 36 carbon atoms, 64 hydrogen atoms and 13 oxygen atoms. The isolated acid has the composition $C_{11}H_{18}O_4$, 2 of its radicals being contained in the antibiotic molecule. From this the total required for the acid is: 22 hydrogen atoms, 36 hydrogen atoms and 8 oxygen atoms. Simple calculation shows that the unknown (not isolated) acid should have the empirical formula $C_{14}H_{28}O_5$. This formula, in which the number of hydrogen atoms is twice the number of carbon atoms, shows that the oxygen atoms of this acid, other than the two carboxyl oxygens, should be bound either as hydroxyl groups or as ether groups. However, the absence of active hydrogen atoms in the antibiotic molecule leads to the conclusion that this acid also has only one hydroxyl group, which, the same as its carboxyl group, participates in the formation of the antibiotic ester groups. All of this suggests that longisporine is a cyclic ester of three hydroxy acids, constructed in accord with the following scheme:



$$\begin{array}{ccc} (C_{10}H_{16}O)-CO-O- & & (C_{10}H_{16}O) \\ | & & | \\ O & & CO \\ | & & | \\ CO- & (C_{13}H_{26}O_2) & -O \end{array}$$

In conlusion we wish to thank N. A. Krasilnikov for supplying us with the *Actinomyces longisporus* culture.

EXPERIMENTAL

Isolation and Purification of Longisporine. Even the first investigations revealed that the main antibiotic mass is found in the mycelium, and not in the water solution; consequently, in obtaining it we took this into consideration and settled on the following method, which was checked on a large laboratory scale.

Twenty liters of the culture liquor with mycelium was vigorously stirred for 1 hour under mechanical stirring with 2 liters of chloroform, and then allowed to stand overnight to settle. By morning the mixture had separated into 3 layers: a top clear water layer (A), then a water layer with mycelium (B), and finally a clear bottom chloroform layer. The latter was separated together with the mycelium-containing water layer (B), and both were again vigorously stirred for 1 hour. Here an emulsion was formed, which was separated by centrifuging (about 2500 r.p.m.). After this the contents of the flasks were poured into a separatory funnel, where the chloroform was separated from the mycelium-containing water layer (C). The chloroform extract dried over sodium sulfate, filtered, and the chloroform removed by distillation. The residue from the chloroform distillation and the mycelium of the water layer (A) were again vigorously stirred for 30 minutes with 4 liters of fresh chloroform. On conclusion of stirring the mixture showed rapid stratification, and the chloroform was separated from the water in a separatory funnel. The chloroform extract (D) was then used to extract the mycelium-containing water layer (C). For this the latter was vigorously stirred for 1 hour with 1 liter of chloroform (D). As in the first case, the resulting emulsion was broken by centrifuging, and the chloroform was separated from the mycelium-containing water layer in a separatory funnel. The chloroform extract was dried and then distilled to remove chloroform, while the mycelium-containing water layer was extracted again with chloroform (D). This operation was repeated 4 times, until all of the chloroform (D) had been consumed. Then the mycelium was discarded, while all of the chloroform extracts were combined and from them on the water bath, at first at atmospheric pressure, and then at the end in vacuo, the chloroform was completely removed by distillation. The residue was a thick dark mass, which when first obtained, could not be crystallized from any solvent. A crystalline antibiotic was first obtained only after its purification with aluminum oxide. For this the noncrystallizing mass remaining after distilling off the chloroform was dissolved in 20 parts of dry ether, and the ether solution was slowly passed through a column filled with aluminum oxide, which had previously been treated with 50% sulfuric acid solution and washed free of the latter with distilled water. After all of the ether solution had been passed through, the column was washed with dry ether. The wash ether was combined with the main solution, and the solvent was completely removed by distillation. The residue was dissolved with heating in the minumum amount of anhydrous alcohol or petroleum ether (b.p. 60-80°) and allowed to stand at 0°. Here large prisms of the crude antibiotic crystallized very slowly (at times a week and longer) from the solution, which, after washing with a mixture of alcohol and ether, melted in the very wide range of 60-70°. Subsequently we were able to obtain a crystalline antibiotic from most of the culture liquors without resorting to the purification with aluminum oxide. In these cases we could achieve crystallization of the substance in concentrated alcohol solutions of 0° by first seeding with a few longisporine crystals.

For final purification of the crude crystalline antibiotic obtained in this manner the latter was first recrystallized 2-3 times with charcoal from 3 parts of anhydrous alcohol, and then 3-4 times without the charcoal from 3 parts of petroleum ether. Usually these recrystallizations were sufficient to give a substance with m.p. 99-101°, remaining constant even after further recrystallizations.

$[\alpha]_D$ + 2.62° (c = 5; chloroform).

Found %: C 66.33, 66.51; H 8.98, 9.08. M (Rast method) 643, 657, 659; (from benzene) 641, 656. $C_{36}H_{58}O_{10}$. Calculated %: C 66.42; H 9.00. M 650.5.

The longisporine yield varied greatly. Evidently, it is strongly dependent on the fermentation conditions. For different series from 20 liters of culture mass (culture liquor with mycelium) the variation in yield ranged from 0 to 1.5 g, based on the pure substance with m.p. 99-101°. At times the culture mass was such that a comparatively large amount of crystalline substance was obtained, which, despite numerous recrystallizations, could not be purified and brought up to the desired melting point of 100°.

Saponification of Longisporine. The ester number was determined in the usual manner. The antibiotic samples taken for analysis weighed approximately 1 g. The saponification was run with 0.5N alcoholic potassium hydroxide solution.

To obtain the hydroxy acid 3 g of longisporine was dissolved in 40 ml of 1N alcoholic potassium hydroxide solution. The solution was boiled for 8 hours under reflux on the water bath; after cooling, a small amount of water was added to it, and all of the alcohol was removed by steam-distillation. The remaining opalescent aqueous solution was made acid to Congo with 20% sulfuric acid solution. The hydrolysis products were extracted with chloroform. The chloroform extract was dried over sodium sulfate, and the chloroform distilled off. A thick yellow oil remained, which, after treatment with a very small amount of benzene—petroleum mixture (1:1) and standing for several days at 0°, partially crystallized. The crystals were separated, washed, and recrystallized from the same mixture. After two recrystallizations the substance was obtained as large snow-white prisms, melting at 64-65°. Further recrystallizations failed to change this melting point. Yield 1.2 g.

Found %: C 61.34, 61.44; H 8.74, 8.78; OH 16.27, 15.47. Equiv 214.3. M (Rast method) 211, 217. $C_{11}H_{18}O_4$. Calculated %: C 61.66; H 8.46; 2OH 15.89. Equiv 214.1. M 214.

To remove excess sulfuric acid, the acid water solution, from which the hydroxy acid had been extracted with chloroform, was treated with a solution of barium hydroxide and together with the precipitate was evaporated to dryness in a dish on the water bath. The dry residue was extracted with alcohol in a Soxhlet apparatus. After distilling off the alcohol we were unable to show the presence of glycerin in the very small amount of residue obtained, even qualitatively (by the formation of acrolein).

SUMMARY

1. A new crystalline antibiotic of composition $C_{36}H_{58}O_{10}$ was isolated from the culture mass (culture liquor with mycelium) of the strain No. 108 *Actinomyces longisporus* (the classification of N. A. Krasilnikov), which we have named longisporine. The latter has: b.p. 99-101° and $[\alpha]_D$ + 2.62°.

2. The combination of the investigated chemical properties of longisporine is evidence that the new antibiotic is a cyclic ester of three hydroxy acids, in structure conforming to the scheme indicated above.

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S. Ordzhonikidze All-Union
Scientific-Research Chemical-Pharmaceutical
Institute

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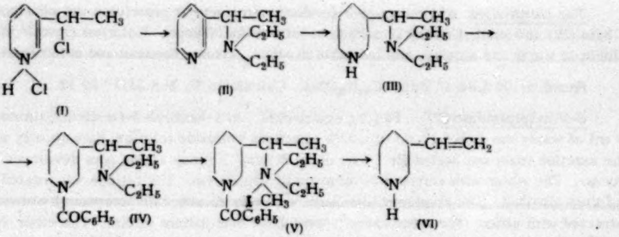
SYNTHESIS OF 3-VINYLPIPERIDINE

L. N. Yakhontov and M. V. Rubtsov

Two schemes are described in the literature for the synthesis of 3-vinylpiperidine (VI): 1) starting from 3-hydroxymethylpiperidine in six steps with a yield of less than 0.5% [1]; and 2) from 3-acetylpyridine in two steps with a yield of about 4% [2]. Both schemes are characterized by extremely low yields of (VI) and both exclude the possibility of adding the propionic acid radical at the 4 position of the piperidine ring, i.e., both schemes are unsuitable for the synthesis of homomeroquinene.

In this paper we describe the synthesis of (VI) from the hydrochloride of 3-(α-chloroethyl)-pyridine by a scheme that might also prove suitable for the synthesis of homomeroquinene.



The starting product was 3-(α-chloroethyl)-pyridine (I), prepared from 3-acetylpyridine [3]. The reaction of (I) with diethylamine gave 3-(α-diethylaminoethyl)-pyridine (II), which under catalytic hydrogenation was transformed into 3-(α-diethylaminoethyl)-piperidine (III). The benzoyl derivative (IV) of the latter was converted into the quaternary salt (V), which was subjected to Hofmann cleavage to give 3-vinylpiperidine (VI). The yield of (VI), based on (I), was 50%. Our product (VI) was identical with the 3-vinylpiperidine described in the literature.

However, the position of the double bond in this compound was not shown experimentally. Moreover it is known that in the attempted preparation of 3-vinylquinuclidine, a compound similar to 3-vinylpiperidine, a shifting of the double bond is observed in most cases with the formation of 3-ethylidene-quinuclidine [4]. Our oxidation of (VI) with potassium permanganate led to the formation of nipecotic acid, which supports structure (VI) as being that of 3-vinylpiperidine.

EXPERIMENTAL

3-(α-Diethylaminoethyl)-pyridine (II). A mixture of 3 g of 3-(α-chloroethyl)-pyridine hydrochloride (I) and 20 g of diethylamine was heated for 10 hours at 120° in a sealed tube. Then the tube contents were treated with 10 ml of 50% potash solution, followed by extraction with ether. The ether extract was dried over potash. The ether and excess diethylamine were vacuum-distilled. The residue distilled at 106-107° (9 mm). Here we obtained 2.6 g (87%) of a pale yellow quite volatile oily substance, readily soluble in the ordinary organic solvents and difficultly soluble in water; n_D^{20} 1.5017.

Found %: N 15.87, 15.57 $C_{11}H_{18}N_2$. Calculated %: N 15.73.

Dihydrochloride: colorless crystals with m.p. 209-210°, readily soluble in water and alcohol and insoluble ether, acetone, chloroform and benzene.

Found %: C 52.39; H 7.89; N 11.11; Cl' 28.48, 28.09. $C_{11}H_{18}N_2 \cdot 2HCl$. Calculated %: C 52.58; H 7.96; N 11.05; Cl' 28.21.

3-(α-Diethylaminoethyl)-piperidine (III). A solution of 4.93 g of 3-(α-diethylaminoethyl)-pyridine dihydrochloride in 75 ml of anhydrous alcohol was hydrogenated in the presence of 0.2 g of Adams platinum catalyst. The hydrogenation was run at room temperature at a pressure of 20-30 cm of water column and was ended in 10 hours. The catalyst was filtered and the filtrate was evaporated in vacuo. The yield of 3-(α-diethylaminoethyl)-piperidine dihydrochloride was 4.99 g, or a quantitative yield. Colorless crystals with m.p. 118-119°, soluble in water, alcohol and chloroform, difficultly soluble in acetone, benzene and toluene, and insoluble in ether. After recrystallization from benzene the melting point of the substance showed no change.

Found %: C 51.32; H 10.28; N 11.19. $C_{11}H_{24}N_2 \cdot 2HCl$. Calculated %: C 51.36; H 10.11; N 10.89.

1-Benzoyl-3-(α-diethylaminoethyl)-piperidine (IV). To a mixture of 5 g of 3-(α-diethylaminoethyl)-piperidine dihydrochloride, 1.1 g of sodium carbonate, 5.5 g of sodium acetate and 20 ml of water was added at 18-20° in 15 minutes with stirring 3.4 g of benzoyl chloride. Stirring was continued for another 5 hours at 18-20°. Then the reaction mixture was treated with 20 ml of 50% potash solution and extracted with chloroform. The chloroform extract was dried over sodium sulfate, and the chloroform was vacuum-distilled. Residue 4.55 g. Its vacuum-distillation gave 4.1 g (73%) of oily substance with b.p. 169-171° (8 mm), n_D^{20} 1.5132, readily soluble in the ordinary organic solvents and insoluble in water.

Found %: C 75.22, 74.92; H 9.62, 9.82; N 9.55. $C_{18}H_{28}ON_2$. Calculated %: C 75.00; H 9.72; N 9.72.

The Methiodide of 1-benzoyl-3-(α-diethylaminoethyl)-piperidine was obtained by boiling a solution of base (IV) and methyl iodide in anhydrous toluene for 36 hours. Colorless crystals with m.p. 121-122°, soluble in water and alcohol, and insoluble in ether, acetone, benzene and chloroform.

Found %: N 6.54; I' 29.66. $C_{19}H_{31}ON_2I$. Calculated %: N 6.51; I' 29.53.

3-Vinylpiperidine (VI). To 1.7 g methiodide of 1-benzoyl-3-(α-diethylaminoethyl)-piperidine in 10 ml of water was added 10 ml of a 50% potassium hydroxide solution; here an oily substance separated. The reaction mass was boiled for 1 hour under reflux. A strong amine odor developed during the boiling process. The water with amines was removed by distillation. The residue was treated with 10 ml of water and then distilled. The combined distillates were treated with 50% potassium hydroxide solution and then extracted with ether. The ether extracts were dried over sodium sulfate. The ether was vacuum-distilled at 20°. The residue (0.4 g) was distilled. The fraction with b.p. 150-155° was collected.* Here we obtained 0.3 g (70%) of a colorless mobile oil, readily soluble in the ordinary organic solvents and in water. The substance contains a double bond (test with potassium permanganate); n_D^{25} 1.4738 [1].

Picrate: yellow crystals with m.p. 161-163° (from alcohol).

Oxidation of 3-Vinylpiperidine. 0.2 g of 3-vinylpiperidine was acidified with 10% sulfuric acid until weakly acid to Congo and then was oxidized by adding in drops, in 3 hours, at 0-5°, a solution of 0.8 g of potassium permanganate in 30 ml of water. During the oxidation the reaction was maintained slightly acid by adding 10% sulfuric acid. The manganese dioxide was filtered and washed with water. The water solution was made alkaline with 10 ml of 16% soda solution and then treated with 0.3 g of benzoyl chloride under stirring. After 6 hours the solution was extracted with ether, then the water layer was acidified with hydrochloric acid and extracted with ether. The ether was removed by distillation. The residue—0.3 g of solid, representing a mixture of 1-benzoyl-nipecotic acid and benzoic acid—was treated with 10 ml of concentrated hydrochloric acid. The obtained mixture was boiled for 8 hours. The benzoic acid was extracted with ether. The aqueous hydrochloric acid solution was evaporated to dryness. The yield of crystalline substance with m.p. 239-240° [5,6] was 0.1 g, being the hydrochloride of nipecotic acid.**

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*Iddes and coworkers [2] give for 3 vinylpiperidine, b.p. 150-155°; picrate, m.p. 162-164° (from benzene). Merchant and coworkers [1] give for 3-vinylpiperidine, b.p. 152-155°, n_D^{25} 1.4731.

**Ladenburg [5] gives for the hydrochloride of nipecotic acid the m.p. 239-240°, and Freudenburg [6] the m.p. 240-241°.

SUMMARY

1. 3-Vinylpiperidine was synthesized in 5 steps from 3-(α-chloroethyl)-pyridine with a yield of 50%, based on reacted products.

2. The position of the double bond in 3-vinylpiperidine was shown by the oxidation of the latter with potassium permanganate to nipecotic acid.

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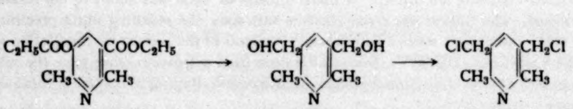
S. Ordzhonikidze All-Union
Scientific-Research Chemical-Pharmaceutical
Institute

SOME β-CHLOROETHYL AND ETHYLENIMINE DERIVATIVES OF PYRIDINE

B. M. Mikhailov and T. K. Kozminskaya

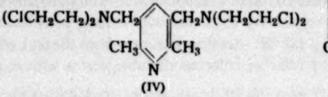
Numerous nitrogen analogs of mustard gas, and also the ethylenimine derivatives of various classes of organic compounds, show antineoplastic properties. Up to now only several compounds of this type have been described in the pyridine series. 4,6-Dimethyl-5-hydroxy-3-β-chloroethylaminomethylpyridine [1] and the bis(β-chloroethyl) amides of nicotinic and isonicotinic acid [2] belong here.

We synthesized some 3,5-disubstituted pyridine derivatives in which the β-chloroethyl and ethylenimine groupings were found in the side chain. The starting compound for the syntheses was 2,6-dimethyl-3,5-di(chloromethyl)pyridine (III), obtained from the diethyl ester of 2,6-dimethyldinicotinic acid (I) by its reduction with lithium aluminum hydride to 2,6-dimethyl-3,5-di(hydroxymethyl)pyridine (II) and subsequent chlorination of the diol by the use of thionyl chloride.



(I) (II) (III)

The synthesis of bis(β-chloroethyl) amines from halo derivatives with a labile halogen is usually accomplished in two steps—condensation of the halo derivatives with diethanolamine and subsequent replacement of the hydroxyl groups by chlorine atoms. We were able to condense the dichloromethyl derivative of pyridine directly with bis(β-chloroethyl)amine and obtain 2,6-dimethyl-3,5-di[bis(β-chloroethyl)aminomethyl]pyridine (IV) in one operation.



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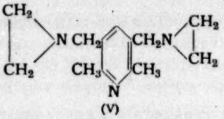
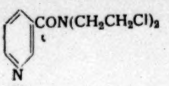


(V)

With ethylenimine in the presence of triethylamine 2,6-dimethyl-3,5-di(chloromethyl)pyridine reacts indifferently and this way 2,6-dimethyl-3,5-di(ethyleniminomethyl)pyridine (V) is obtained in poor yield. The condensation of (III) is smoother with sodioethylenimine.

We also synthesized the bis(β-chloroethyl) amides of nicotinic (VI) and isonicotinic (VII) acid by reacting the chlorides of the corresponding acids with bis(β-chloroethyl)amine. These compounds were obtained by us prior to the appearance in print of the communication by Drefahl and König [3], who synthesized the hydrochlorides of the above mentioned amides by condensing the esters of nicotinic and isonicotinic acid with diethanolamine and subsequent halogenation of the hydroxyethyl derivatives by means of thionyl chloride [2].



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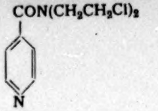

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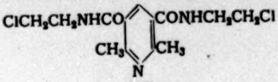

(VIII)

The condensation of the diethyl ester of 2,6-dimethyldinicotinic acid with ethanolamine gave the di-β-hydroxyethylamide of 2,6-dimethyldinicotinic acid, which with thionyl chloride was converted to the di-β-chloroethylamide of 2,6-dimethyldinicotinic acid (VIII).

EXPERIMENTAL

2,6-Dimethyl-3,5-di(hydroxymethyl)pyridine (II). 2,6-Dimethyl 3,5-dicarbethoxypyridine was reduced with lithium aluminum hydride by the method proposed by Bohlmann [3], but with some modifications: the mixture of starting ester and lithium aluminum hydride after being heated fo 2 hours was allowed to stand to the next day; a small amount of water was used for the decomposition; the final product was recrystallized from water. 2,6-Dimethyl-3,5-di(hydroxymethyl)pyridine with m.p. 134-137° was obtained in 79% yield. The pure product melts at 141-142°, which agrees with the literature.

2,6-Dimethyl-3,5-di(chloromethyl)pyridine (III). To 6 ml of thionyl chloride at 0° was added in small portions 1.5 g of 2,6-dimethyl-3,5-di(hydroxymethyl)pyridine. The reaction mixture was heated at the boil for 1.5 hours. The excess thionyl chloride was vacuum-distilled; its traces were removed by adding benzene to the residue and vacuum-distilling the solvent. A small amount of water was added to the residue, and the aqueous solution was filtered. The filtrate was made alkaline with soda, the resulting white precipitate was extracted with ether, and the ether extract was washed with water. Removal of the solvent by distillation gave 1.56 g (86.2%) of crystalline residue with m.p. 105-107°. Recrystallization from petroleum ether gave the substance as elongated prisms with m.p. 107-108.5°. 2,6-Dimethyl-3,5-di(chloromethyl)pyridine is readily soluble in most organic solvents.

Found %: C 52.92, 52.95; H 5.49, 5.44; N 6.93; Cl 34.80. $C_9H_{11}NCl_2$. Calculated %: C 52.96; H 5.43; N 6.86; Cl 34.74.

2,6-Dimethyl-3,5-di[bis(β-chloroethyl)aminomethyl]pyridine (IV). To a solution of 2 g of 2,6-dimethyl-3,5-di(chloromethyl)pyridine in 5 ml of benzene was added a benzene-chloroform solution of bis(β-chloroethyl)-amine, prepared from 8 g of bis(β-chloroethyl)amine hydrochloride [4], and 2 drops of pyridine. The reaction mixture was boiled on the water for 60 hours, and the resulting precipitate was filtered and washed with benzene. After recrystallization from an acetone-alcohol mixture the substance melted at 216-217°, and failed to depress the melting point when mixed with bis(β-chloroethyl)amine hydrochloride. The benzene-chloroform extract was evaporated in vacuo. The oily residue was repeatedly extracted with boiling petroleum ether. The yield of crystalline substance with m.p. 93-100° was 0.9 g (22 %). Recrystallization from diethyl ether gave the 2,6-dimethyl-3,5-di[bis(β-chloroethyl)aminomethyl]pyridine as colorless rhombic plates with m.p. 99-100°.

Found %: C 49.03, 48.91; H 6.58, 6.62; Cl 34.0, 34.28. $C_{17}H_{27}N_3Cl_4$. Calculated %: C 49.17; H 6.55; Cl 34.15.

2,6-Dimethyl-3,5-di(ethyleniminomethyl)pyridine (V). To a solution of 5.1 ml of ethylenimine in 35 ml of absolute ether, contained in a 4-necked flask, was added with stirring 3 g of powdered sodium amide. The reaction mixture was stirred for an hour at room temperature, and then for an hour at 26-30°. To the reaction mixture, cooled to −10°, with vigorous stirring was cautiously added an ether solution of 4.75 g of 2,6-dimethyl-3,5-di(chloromethyl)pyridine (60 ml), in which connection the temperature was maintained at −5 to −7°. After all of the solution had been added the reaction mixture, cooled with ice, was stirred another 30 minutes, and then filtered. The precipitate on the filter was washed with ether. The ether filtrate was evaporated in vacuo at room temperature. The oil residue was repeatedly extracted with petroleum ether. Removal of the solvent gave 1.9 g (31%) of crystalline substance with m.p. 60-67°, proving to be free of halogen. Further purification by extraction with petroleum ether and subsequent recrystallization from diethyl ether gave the substance, extremely volatile with the solvent vapors, as colorless needles with m.p. 71-72°.

Found %: N 19.22, 18.96. $C_{13}H_{19}N_3$. Calculated %: N 19.33.

Bis(β-chloroethyl)amide of Isonicotinic Acid (VII). A mixture of 9.5 g of isonicotinic acid and 20 ml of thionyl chloride was heated to dissolve the acid, and the solution was boiled for 20 minutes. The excess thionyl chloride was vacuum-distilled. To the obtained isonictinoyl chloride hydrochloride was added 15 ml of dry benzene and the obtained suspension was treated with a benzene-chloroform solution of bis(β-chloroethyl)amine, obtained from 13 g of its hydrochloride [4].

The reaction mass was boiled for 3 hours. The obtained precipitate of bis(β-chloroethyl)amine hydrochloride (7.1 g) was filtered, and the filtrate was evaporated in vacuo. The yield of substance with m.p. 91-94° was 4.2 g (90%). After recrystallization from ethanol the substance had m.p. 95-97°.

Found %: C 48.55, 48.60; H 5.08, 5.14; N 11.68; Cl 28.69. $C_{10}H_{12}ON_2Cl_2$. Calculated %: C 48.60; H 4.93; N 11.33; Cl 28.69.

Bis(β-chloroethyl)amide of Nicotinic Acid (VI). The bis(β-chloroethyl)amide of nicotinic acid was obtained in a similar manner from 5 g of nicotinic acid. The yield of light-yellow crystalline substance with m.p. 59-64° was 5.9 g (64%). After recrystallization from a mixture of benzene and petroleum ether the substance had m.p. 62-64°.

Found %: N 11.61, 11.56. $C_{10}H_{12}ON_2Cl_2$. Calculated %: N 11.33.

Di-β-hydroxyethylamide of 2,6-Dimethyldinicotinic Acid. A mixture of 20 g of 2,6-dimethyl-3,5-dicarbethoxypyridine, 25 ml of ethanolamine and 2-3 drops of pyridine was heated for 3 hours at 180°. The obtained precipitate was filtered and washed on the filter with anhydrous ethanol. The yield of colorless crystalline product with m.p. 185-187° was 19.3 g (86%). After recrystallization from ethanol the substance had m.p. 189-190°.

Found %: C 55.44, 55.33; H 6.72, 6.83. $C_{13}H_{19}O_4N_3$. Calculated %: C 55.51; H 6.80.

Di-β-chloroethylamide of 2,6-Dimethyldinicotinic Acid (VIII). To a suspension of 10.5 g di-β-hydroxyethylamide of 2,6-dimethyldinicotinic acid in 35 ml of chloroform, cooled to 0°, was added with stirring a solution of 6 ml of thionyl chloride in 20 ml of chloroform. The next day the reaction mixture was heated on the water bath for 2 hours. The precipitate was filtered and washed with chloroform, benzene and ether, The yield of substance with m.p. 220-224° was 14.2 g. Recrystallization from ethanol gave 11.3 g (85%) of di-β-chloroethylamide of 2,6-dimethyldinicotinic acid with m.p. 227-229°.

Found %: N 11.89, 11.89; Cl 30.18, 30.17. $C_{13}H_{18}O_2N_3Cl_3$. Calculated %: N 11.85; Cl 29.99.

The base, obtained from the above described salt and recrystallized from ethanol and from acetone, melted at 178-179°.

Found %: C 49.32; H 5.51, 5.50; N 13.27, 13.40. $C_{13}H_{17}O_2N_3Cl_2$. Calculated %: C 49.07; H 5.38; N 13.23.

SUMMARY

The preparation of 2,6-dimethyl-3,5-di[bis(β-chloroethyl)-aminomethyl]pyridine and 2,6-dimethyl-3,5-di(ethyleniminomethyl)-pyridine, and also of some β-chloroethyl derivatives of the amides of nicotinic, isonicotinic and 2,6-dimethyldinicotinic acid, was described.

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Received June 20, 1955

Found %: N [illegible] Calculated %: N [illegible]

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Found %: C [illegible]

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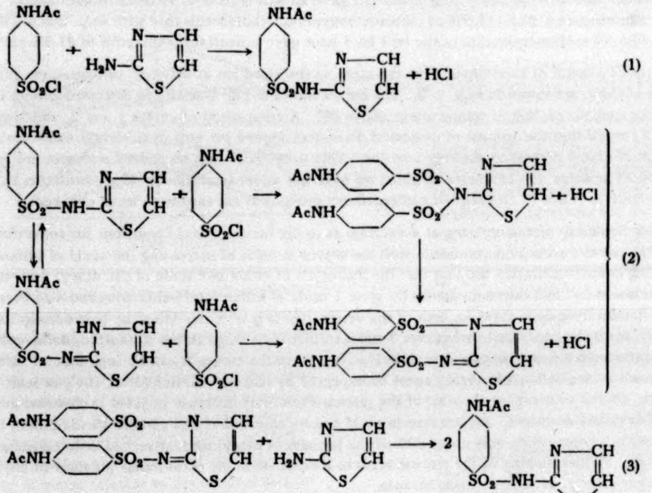
REACTION OF ACYLSULFANILYL CHLORIDES WITH 2-AMINOTHIAZOLE

I. REACTION OF DI-(CARBOMETHOXYSULFANILYL)-AMINOTHIAZOLE WITH 2-AMINOTHIAZOLE

B. G. Yasnitsky and E. B. Dolberg

Based on a comparison of some literature data [1] it follows that the main reactions in the acylation of 2-aminothiazole with acylsulfanilyl chlorides can be depicted by the scheme.



where Ac is either the acetyl or formyl radical, or carbonic acid esters.

The end reaction product is usually a mixture of the acylsulfanilylaminothiazole (in the future the monoacyl derivative) and di-(acylsulfanilyl)-aminothiazole (in the future the diacyl derivative). The liberated hydrogen chloride is bound either with excess 2-aminothiazole or with some other specially introduced base.

Our problem was to study the influence of certain factors on the yield and ratio of the mono- and diacyl derivatives formed in the reaction between carbomethoxysulfanilyl chloride and 2-aminothiazole.

To judge the relative reaction rates of reactions (1), (2) and (3) we first studied the kinetics of the reaction for converting the diacyl derivative into the monoacyl derivative (reaction 3), a discussion of which is the subject of the present communication. The reaction was run in a medium of dry inert organic solvents in accord with the method that we had proposed earlier [2].

EXPERIMENTAL

The starting 2-aminothiazole had m.p. 89-90°. Its purity by acidometric analysis was 99.5-100.0%. Di-(carbomethoxysulfanilyl)-aminothiazole was obtained by reacting carbomethoxysulfanilyl chloride with a water solution of the aminothiazole hydrochloride. The reaction product was separated from carbomethoxysulfanilylaminothiazole and sulfanilic acid by treatment with 2% sodium hydroxide solution. The gray-yellow powder with m.p. 188°, after recrystallization from alcohol, melts at 196-197° with charring. The organic solvents that we used were dried over fused sodium sulfate and distilled in the limits of 1-2°.

The method of running the experiments is typified by the example: to 100 ml of chlorobenzene, heated to 120°, was added 3.0 g of 2-aminothiazole and 15.78 g of the diacyl derivative: the heating was for 1 hour under reflux with mechanical stirring at 130°. The cooled reaction product was separated from the chlorobenzene, washed with 100 ml of 2% hydrochloric acid, heated to 50°, and then with water until all of the aminothiazole had been removed. The dry precipitate weighed 14.5 g. Alkalimetric titration of the mother liquors and wash waters, using methyl orange and phenolphthalein as indicators, established the presence of 2.01 g of the aminothiazole (67% of the amount taken for reaction). Five grams of the obtained precipitate was treated with a 2% sodium hydroxide solution. The residue was 3.60 g or 66.2% of the introduced di-(carbomethoxysulfanilyl)-aminothiazole with m.p. 190.0°. Its hydrolysis gave an 87.0% yield of sulfanilamidothiazole. Neutralization of the filtrate gave 1.25 g (19.3%) of carbomethoxysulfanilylaminothiazole with m.p. 236.5°, the hydrolysis of which with 9% sodium hydroxide at the boil for 1 hour gave sulfanilamidothiazole in 87.9% yield.

The results of a series of experiments, run the same as described but at different temperatures and for various periods of time, are shown in Figs. 1-3; The curves shown in Fig. 1 testify to the considerable increase in the rate of the studied reaction at temperatures above 80°. A comparison of curves 1 and 2, and also of 3 and 4, in Fig. 2 reveals that the amount of monoacyl derivative, formed per unit of time, lags considerably behind the amount of diacyl derivative showing reaction. This is evidence that secondary processes are present, leading to a loss of products, the character of which we have not as yet established. The postulation that the loss of acyl derivatives is due to cleavage of carbomethoxy groups was not supported when checked.

Fig. 3 is presented to permit arriving at a decision as to the most rational conditions for converting the diacyl derivative into the monoacyl compound with the object in mind of increasing the yield of sulfanilamidothiazole. Taking into consideration the fact that the hydrolysis of either one mole of the diacyl derivative or one mole of the monoacyl derivative theoretically gives 1 mole of sulfanilamidothiazole, and also bearing in mind the fact that the hydrolysis yield for both of the derivatives is practically the same (see description of the experiment), it can be concluded that curves 3 and 6 reflect the change in the sulfanilamidothiazole yield in percent of that obtained from the pure diacyl derivative. From the curves it can be seen that an essential increase in the sulfanilamidothiazole yield cannot be expected by running reaction (3) at 100°, at least not in the first 5 hours. On the contrary, at the start of the process even some decrease in yield is observed due to the progress of secondary reactions. An increase in yield can be observed at 130°, where its maximum is achieved after approximately 3 hours, when only about 60% of the introduced diacyl derivative had been consumed for reaction (curve 5). Further running of the process leads to a decrease in the total molar amounts of acyl derivatives, and consequently, of sulfanilamidothiazole.

As can be seen from Fig. 3, the maximum increase in yield is far from theory for the complete conversion of the diacyl derivative into the monoacyl compound (200%) and represents only 135% of this amount, which can also be obtained directly from the diacyl derivative.

The experimental points, reflecting the sulfanilamidothiazole yield as a result of hydrolyzing mixtures of the acyl derivatives (obtained at 130° for various periods of time), referred to the amount of sulfanilamidothiazole (obtained directly from the diacyl derivative), fall quite well on curve 6, which was constructed as the graphical sum of curves 4 and 5. Considerable tarring of the introduced 2-aminothiazole is observed when reaction (3) is run above 130°.

From the experimental data we calculated the rate constants for the formation of the monoacyl derivative (reaction 3), using the formula for second order reaction; their average values proved to be: at 100°–

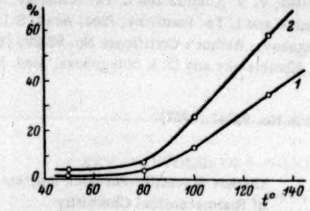


Fig. 1. Dependence of the yield (in %) of carbomethoxysulfanilylaminothiazole (1) and composition of the product (in mole%) of the monoacyl derivative (2) on the temperature of the process, run for 2 hours.

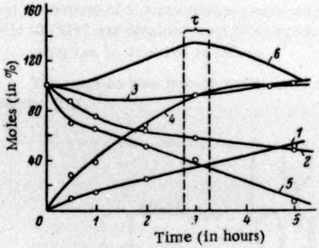


Fig. 3. Relationship between the sulfanilamidothiazole yield and the reaction time of di(carbomethoxysulfanilyl)-aminothiazole with 2-aminothiazole.
1) and 4) amount of formed monoacyl derivative,
2) and 5) amount of remaining diacyl derivative,
3) and 6) total molar amounts of acyl derivatives. [1,2 and 3) at 100°, 4,5, and 6) at 130°].
Along the ordinate are plotted in percent the number of moles relative to the original number of moles of the diacyl derivative, the latter taken as 100%.

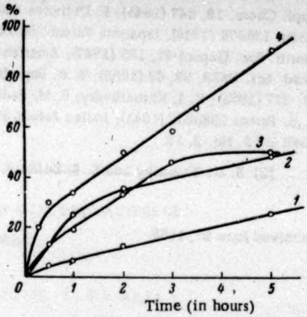


Fig. 2. Kinetics of the reaction of di-(carbomethoxysulfanilyl)-aminothiazole with 2-aminothiazole in chlorobenzene.
1) and 3) yield of monoacyl derivative (in %),
2) and 4) consumption of diacyl derivative in percent of initial amount [1 and 2) at 100°, 3 and 4) at 130°].

$(1.32 \pm 25\%) \cdot 10^{-3}\ \mathrm{mol}^{-1}\ \mathrm{minute}^{-1}$ and for 130°–$(4.41 \pm 21\%) \cdot 10^{-3}\ \mathrm{mol}^{-1}\ \mathrm{minute}^{-1}$. the relatively large variations are explained by the presence of secondary reactions and the inadequate accuracy of the analytical methods. Nevertheless, since the extreme values did not deviate from the average by more than 25%, whereas the average values for 100 and 130° differ by a factor of 3.34, we considered the average values of the constants as approximate, and on this basis calculated the approximate value of the energy of activation for the studied process, which equaled 12,000 cal.

SUMMARY

1. In its role as a main reaction taking place in the acylation of 2-aminothiazole with carbomethoxysulfanilyl chloride in chlorobenzene, the kinetics of the reaction of di-(carbomethoxysulfanilyl)-aminothiazole with 2-aminothiazole was studied.

2. Due to secondary processes it was established that here the yield of carbomethoxysulfanilylaminothiazole is considerably below the theoretical.

3. The relationship between the change in the sulfanilamidothiazole yield and the length of running the studied process at 100 and 130° was found from an analysis of the kinetics curves.

4. The approximate values of the rate constants for the formation of carbomethoxysulfanilylaminothiazole from di-(carbomethoxysulfanilyl)-aminothiazole at 100 and 130° were calculated, as was also the energy of activation for the process.

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Kharkov Scientific-Research Institute
of Pharmaceutical Chemistry

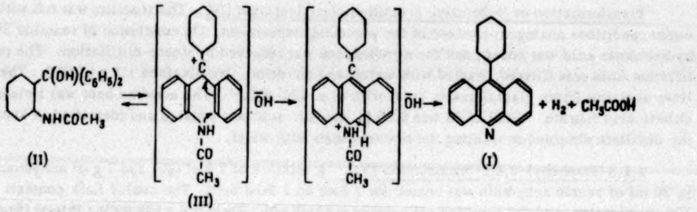
CHEMISTRY OF HETEROCYCLES

XXV. SYNTHESIS OF 9-PHENYLACRIDINE FROM ACYL DERIVATIVES OF 2-AMINOTRIPHENYLCARBINOL

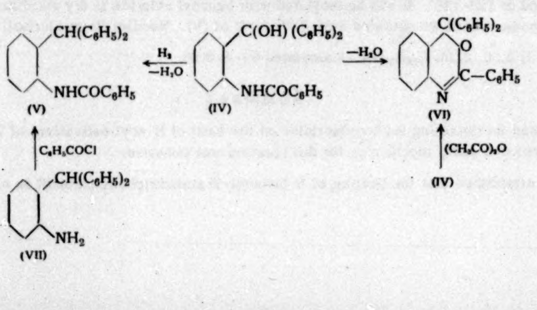
P. A. Petyunin, N. G. Panferova and M. E. Konshin

In a previous communication [1] we described a preparative method for obtaining 9-phenylacridine based on 2-aminotriphenylcarbinol. In the present study our problem was to synthesize 9-phenylacridine (I) from the acyl derivatives of 2-aminotriphenylcarbinol. The experiments were run in nitrobenzene medium, and the highest yield (I) (71%) was obtained from N-acetyl-2-aminotriphenylcarbinol (II). As applied to the latter the reaction mechanism can be depicted as follows.

The reaction goes through the dissociation stage (II) and the acridine cycle suffers closure into the ionic complex (III).


C(OH)(C6H5)2
NHCOCH3
(II)
+C
NH
CO
CH3
(III)
ŌH→
C
+NH H
CO
CH3
ŌH→
N
(I)
+ H2 + CH3COOH

In contrast to (II) the transformation of N-benzoyl-2-aminotriphenylcarbinol (IV) proceeds by a more complicated scheme. Among the reaction products, other than (I) (yield 38.7%) and benzoic acid, the formation of water was shown and a substance with m.p. 220-221.5° (yield 58.1%) was isolated. Proceeding from the fact that water is liberated during reaction the substance with m.p. 220-221.5° can be assigned the structure of N-benzoyl-2-aminotriphenylmethane (V) or 1,1,3-triphenyl-2,4,1-benzoxazine (VI):


CH(C6H5)2
NHCOC6H5
(V)
H2
−H2O
C(OH) (C6H5)2
NHCOC6H5
(IV)
−H2O
C(C6H5)2
O
C—C6H5
N
(VI)
C6H5COCl
CH(C6H5)2
NH2
(VII)
(CH3CO)2O
(IV)

The formation of (V) can be assumed if it is considered that hydrogen is evolved in the transformation of (IV) into 9-phenylacridine.

Based on the analysis data it is very difficult to give preference to one of these structures. We decided to prove the structure of the substance with m.p. 220.221.5° by counter synthesis. Thus, the benzoylation of 2-aminotriphenylmethane (VII) gave (V), which proved to be different in its properties from our studied substance. Also in disfavor of (V) is the fact that the substance with m.p. 220-221.5° fails to liberate methane when treated with methylmagnesium iodide.

The conclusion that the substance with m.p. 220-221-5° shows structure (VI) was made on the basis of comparing it with the authentic specimen. The latter was obtained by treating (IV) with acetic anhydride in the presence of anhydrous sodium acetate. As a result, it was established that the heating of (IV) in nitrobenzene medium yields two compounds, in which connection the main reaction product is the benzoxazine derivative (VI).

EXPERIMENTAL

N-Benzoyl-2-aminotriphenylcarbinol (IV). To a solution of 5 g of 2-aminotriphenylcarbinol in 15 ml of dry pyridine was added 2.8 g (10% excess) of benzoyl chloride. After heating for an hour on the water bath the flask contents were poured into 100 ml of water, and the reaction product was isolated in the usual manner. Yield 4 g (57.2%). Fine crystalline powder (from glacial acetic acid) with m.p. 211-213°.

Found %: N 3.79, 3.64. $C_{26}H_{21}O_2N$. Calculated %: N 3.69.

9-Phenylacridine (I). A solution of 1 g of (II) in 1 ml of nitrobenzene was boiled on a sand bath for 30 minutes. After cooling, 15 ml of dilute hydrochloric acid was added and the nitrobenzene was steam-distilled. The acridine base was isolated from the hydrochloric acid solution by the addition of ammonia. Yield 0.62 g. Needles (from alcohol) with m.p. 184-186°; picrate, m.p. 227-229°.

Literature: b.p. 184° [2]; picrate b.p. 227.7° [3].

Transformation of N-Benzoyl-2-aminotriphenylcarbinol (IV). The reaction was run with 2 g of (IV) and under conditions analogous to those of the preceding experiment. On conclusion of reaction 30 ml of dilute hydrochloric acid was added, and the nitrobenzene was removed by steam-distillation. The residue in the distillation flask was filtered, washed with water, and air-dried. We obtained 1.1 g of (VI). The substance crystallizes as prisms (from glacial acetic acid) with m.p. 220-221.5°. The acridine base was isolated from the hydrochloric acid filtrate. Yield of (I) was 0.52 g. Benzoic acid was isolated and identified in known manner from the distillate obtained in treating the reaction mass with water.

1,1,3-Triphenyl-2,4,1-benzoxazine (VI). A mixture of 7 g of (IV) and 7 g of anhydrous sodium acetate in 30 ml of acetic anhydride was heated for 1 hour on a sand bath. The cooled flask contents were poured into 100 ml of water, and the resulting oil quickly crystallized. Yield 6.6 g (99.09%). Prisms (from glacial acetic acid) with m.p. 220-221.5°. Its mixed melting point with the substance (m.p. 220-221.5°) obtained in the preceding experiment was not depressed.

Found %: C 86.39, 86.29; H 5.3, 5.31; N 4.01, 3.85. $C_{26}H_{19}ON$. Calculated %: C 86.33; H 5.23; N 3.87.

Picrate (VI) was obtained by mixing the benzene solutions. M.p. 206.5°.

N-Benzoyl-2-aminotriphenylmethane (V). 2-Aminotriphenylmethane (VII) was obtained by the method of [4], and melted at 128-130°. It was benzoylated with benzoyl chloride in dry pyridine solution. From 4.07 g of 2-aminotriphenylcarbinol we obtained 5.55 g (97.19%) of (V). Needles (from alcohol) with m.p. 149-149.5°.

Found %: N 3.96, 3.94. $C_{26}H_{21}ON$. Calculated %: N 3.85.

SUMMARY

1. A method for obtaining 9-phenylacridine on the basis of N-acyl derivatives of 2-aminotriphenylcarbinol was developed and a mechanism for this reaction was discussed.

2. It was established that the heating of N-benzoyl-2-aminotriphenylcarbinol in nitrobenzene medium

gives, besides the 9-phenylacridine, 1,1,3-triphenyl-2,4,1-benzoxazine as the main reaction product.

3. The new N-benzoyl-2-aminotriphenylcarbinol, 1,1,3-triphenyl-2,4,1-benzoxazine and N-benzoyl-2-aminotriphenylmethane were prepared and described.

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Molotov Pharmaceutical Institute

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* T.p. = C. B. Translation pagination.

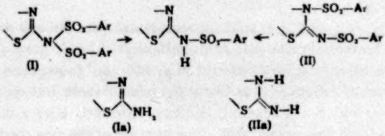
THE STRUCTURE OF THIAZOLE DISULFAMIDES

I. Ya. Postovsky and V. V. Kushkin*

As is known, sulfanilamide compounds of pyridine, pyrimidine and thiazole are obtained by reacting the α-amino derivative of the corresponding heterocycle with the p-acylaminobenzenesulfonyl chloride. If the reaction is run in aqueous-alkaline medium [1] or in pyridine in the cold [2], then the diacylsulfanilamide compound ("disulfamide") is formed. An acylsulfanilyl radical of disulfamide is easily cleaved when the latter is heated in alkaline medium, and here the other radical shows only deacylation and remains on the nitrogen of the amino group in the 2 position of the heterocycle. The position of this sulfanilyl radical, e.g. in sulfanilamidopyridine, is shown by synthesis from 2-bromopyridine and the sulfanilamide Na salt [3].

Two different structures (I and II) can be assumed for disulfamides, corresponding to the two tautomeric forms of the α-amino-N-heterocycle (Ia, IIa) (Scheme 1).

Scheme 1



Disulfamides are usually assumed to have structure (II) [1,2,4,5,6], but at times structure (I) is also presented [7]. For example, structure (I) has been shown for the disulfamide obtained from 4-amino-2,6-dimethylpyrimidine [8]. The possibility of a disulfamide migrating from one structure to the other is also admissible. Thus Deliwala and coworkers [9] on reacting acetylsulfanilyl chloride with 2-aminothiazole in pyridine obtained a disulfamide with m.p. 127-129°, to which they assign structure (I); when heated in alcohol solution the substance migrates into a stable compound with m.p. 190-225°, for which structure (II) is given. Here attention is drawn to the extremely wide melting range shown by the stable form of the disulfamide.** Apparently, the reason for this lies either in the heterogeneity of the substance or in the transformations that occur during heating when the melting point is being determined. A similar spread in the melting point of the same substance, at times exceeding 50°, is mentioned by various authors [10]. Angyal [11] was able to obtain certain disulfamides in two forms with different melting points, in which connection he assumes structure (II) for disulfamides and explains the presence of two forms as due to geometric isomerism at the C = N bond.

The presented data serve as evidence that the question as to the structure of disulfamides cannot be considered solved. In addition it is of undoubted interest for the manufacture of sulfanilamide compounds, as well as for the important theoretical question of the tautomerism shown by 2-amino-N-heterocycles, a subject that has frequently been touched upon by both Soviet [12-16] and foreign authors [17,18]. In this communication we examine the structure of certain thiazole disulfamides, since they proved to be the most frequent discussion topic.

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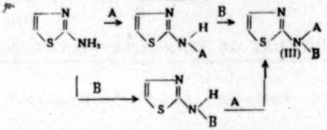
* From the Candidate's Dissertation of V. V. Kushkin "On the Tautomerism of 2-Aminothiazole and Some of Its Derivatives" (Sverdlovsk, 1954).

** Other authors [4,6,7] also give a melting point range of 20-50° for this compound.

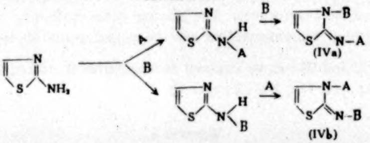
We obtained the disulfamides by introducing various sulfaryl radicals (A,B) in the 2-aminothiazole molecule and compared their properties. Successive introduction of various sulfaryl radicals should have led to different compounds, depending on whether the disulfamide had structure (I) or (II). If two different sulfaryl radicals, A and B, replace both hydrogens in the amino group of 2-aminothiazole, then independent of the order in which the radicals are introduced a disulfamide with the same thiazole structure (III) is obtained (Scheme 2).

Scheme 2



If the sulfaryl radicals (A,B) become attached to different nitrogen atoms, then depending on the order of their introduction, a disulfamide with two different thiazole structures (IV^a) and (IV^b) is obtained (Scheme 3).

Scheme 3



The reaction of 2-aminothiazole with p-chlorobenzenesulfonyl chloride and subsequent reaction of the obtained 2-(p-chlorobenzenesulfamido)thiazole with acetylsulfanilyl chloride gave a disulfamide, which after a number of recrystallizations from alcohol showed constant m.p. 164-166° (compound "a"). The other disulfamide was obtained with a different order of introducing radicals: 2-aminothiazole was successively condensed first with acetylsulfanilyl chloride, and then with p-chlorobenzenesulfonyl chloride. Here a disulfamide with constant melting point (162-164°) was obtained (compound "b"). The mixture of the two products melted at 158-160°. As can be seen from these data, the melting points of the two disulfamides are very close, and the melting point depression of their mixture is small; consequently, on the basis of the melting point determinations it is difficult to say with assurance whether the obtained products are the same or different, and for the same reason whether their structure is the same or different.

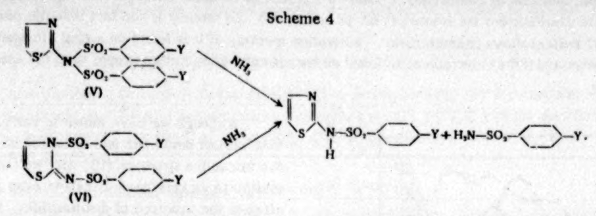
In connection with this we synthesized another pair of disulfamides, already mentioned in the literature. By reacting 2-(benzenesulfonamido)thiazole with acetylsulfanilyl chloride in acetone medium in the presence of potassium bicarbonate Ohta [5] obtained a disulfamide with m.p. 162-163°, and by reacting 2-(acetylsulfanilamido) thiazole with benzenesulfonyl chloride, a substance with 168-170°. When these reactions were run in pyridine in the cold we obtained products with different melting points. The first disulfamide melted constant at 143-145° (compound "c"), the second at 156-158° (compound "d"), while the mixture melted at 136-138°. As can be seen, the melting points of this pair of compounds show a greater difference than do the pair of the preceding case, and here the melting point depression of the mixture is considerable. This suggests structure (II) for the obtained disulfamides. However, here also the difference in the melting points from those given in the literature did not permit making a decisive conclusion as to the structure of disulfamides.

To solve the problem of the structure of the isolated disulfamides we made use of the ammonolysis method, which was first described for disulfamides by V. I. Khmelevsky and coworkers [19]. The ammonolysis of a diacylsulfanilamidothiazole gives two readily separated products– the soda-soluble 2-(p-acylsulfanilamido)thiazole ("acylsulfothiazole") and the soda-insoluble p-acylsulfanilamide.

If in a disulfamide two sulfaryl radicals are alike (in each a Y group may be found in the para position) (Scheme 4), then in the ammonolysis of both disulfamide with structure (V) and disulfamide with structure (VI)

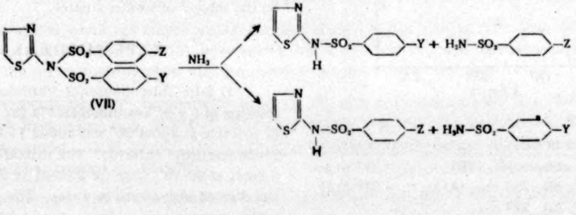
the same products are obtained, and to judge the disulfamide structure on the basis of the ammonolysis results will be impossible.

Scheme 4

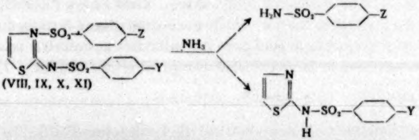


If, as in our case, the radicals are different (in one, a Y group is found in the para position, and in the other a Z group) (Schemes 5 and 6), then, depending on whether the disulfamides are constructed on the type of (I) (Scheme 5) or on the type of (II) (Scheme 6), different ammonolysis products are obtained.

Scheme 5



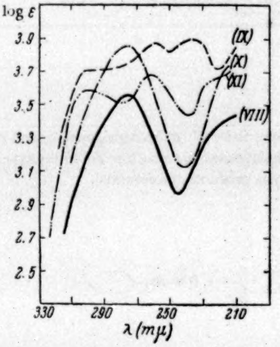
Scheme 6



(VIII) $Y = Cl$; $Z = NHCOCH_3$.
(IX) $Y = NHCOCH_3$; $Z = Cl$.
(X) $Y = H$; $Z = NHCOCH_3$.
(XI) $Y = NHCOCH_3$; $Z = H$.

The ammonolysis of the above discussed disulfamide "a" (m.p. 164-166°) gave two sulfamides, different from the two sulfamides obtained from compound "b" (m.p. 162-164°). In complete accord with Scheme 6, two different pairs of sulfamides were also obtained from compounds "c" and "d". Judging from the melting points and properties of the obtained ammonolysis products (see "Experimental") the remaining radical linked with the thiazole ring is the one that was introduced first; from this structure (VIII) ensues for compound "a", structure (IX) for compound "b", and correspondingly, (X) for "c" and (XI) for "d".

As a result, on the basis of studying the ammonolysis products it can be concluded that the disulfamides isolated from the reaction medium have the thiazoline structure (II), and not the thiazole structure (I). This conclusion is operative only if during the ammonolysis process itself there is not any previous rearrangement of (I) → (II) during heating in an ammoniacal medium. In order to pin down this problem it was necessary to examine the structure of the obtained substances by other than chemical reaction. For this we studied the absorption spectra of the disulfamides in the ultraviolet. If, outside of reaction, compounds "a" and "b" were identical, i.e., they both had a type (I) structure, then their absorption spectra should coincide. Actually, the absorption spectra of these compounds, and also of compounds "c" and "d", proved to be quite different (see Figure), i.e., also outside of reaction these disulfamides are isomers (VIII, IX and X, XI). Of interest is the fact that the position of the acetylsulfanilyl radical shows characteristic absorption spectra. If it is found on a ring nitrogen, then only one maximum appears, and if the same radical is found on the nitrogen of an amino group, then the spectrum shows three maxima.



Absorption spectra in dioxane solution (concentration $5 \cdot 10^{-4}$M) of the compounds: (VIII) λ_{max} = 277 m μ; (IX) λ_{max} = 300, 261, 239 mμ; (X) λ_{max} = 277 mμ; (XI) λ_{max} = 296, 261, 227 mμ.

Although we have shown in the present study that without doubt the four obtained disulfamides have the thiazoline structure (II), still we consider it premature to make a generalization from these data relative to the structure of disulfamides. For example, there still remains unanswered the question as to the reasons for the formation of disulfamide compounds with two different or extremely extended melting points. Whether this is due to cis, trans isomerism at the C═N bond [11], crystallographic dimorphism, characteristic of some sulfamides [20], or finally, transitions of form (I) → (II), and at times of (II) → (I), it should be the subject of further studies.

EXPERIMENTAL

1) 2-(p-Chlorobenzenesulfamido)thiazole. To a solution of 6 g of 2-aminothiazole (m.p. 88°) in 18 ml of pyridine at about 25° was added 12.6 g of p-chlorobenzenesulfonyl chloride. The mixture was heated for 3 hours at 60-70°, then for 2 hours at 90-95°, cooled, and diluted with 50 ml of water. The resulting light-yellow precipitate was filtered, washed with water, and dried. Yield 12.5 g (76.9%). Dissolving in warm alkali and subsequent cooling gave the crystalline Na salt, which was recrystallized 3 times from water. Treatment of the water solution of the salt with hydrochloric acid gave the sulfamide as colorless prisms. Yield 8 g (48.7%). From alcohol the compound crystallizes as large colorless elongated prisms with m.p. 198-199°.

Found %: N 9.77. $C_9H_7O_2N_2ClS_2$. Calculated %: N 10.02.

2) 2-(p-Chlorobenzenesulfonimido)-3-(acetylsulfanilyl)-4-thiazoline (VIII). To a solution of 5.5 g of 2-(p-chlorobenzenesulfamido)thiazole in 15 ml of pyridine was gradually added at 20-25° 4.7 g of freshly recrystallized (from dichloroethane) acetylsulfanilyl chloride. After standing for 8 hours the thick light-yellow reaction mass was diluted with 70 ml of water, and the resulting precipitate was filtered: Yield 7.7 g (74.2%), m.p. 160-162°. Recrystallizations from alcohol gave coarse prisms with constant m.p. 164-166°. The substance is insoluble in dilute acids and alkalies, difficultly soluble in alcohol, and less difficultly soluble in pyridine and acetone.

Found %: N 9.07; S 20.24; Cl 7.67. $C_{17}H_{14}O_5N_3ClS_3$. Calculated %: N 8.90; S 20.38; Cl 7.51.

3) 2-Acetylsulfanilylimido-3-(p-chlorobenzenesulfonyl)-4-thiazoline (IX). To a suspension of 8.9 g of the acetylsulfothiazole in 20 ml of pyridine was added 4.2 g of p-chlorobenzenesulfonyl chloride, and the reaction mixture was let stand 3 hours at room temperature. Then the mixture was poured into dilute NaOH solution. The resulting precipitate was filtered and washed with water until the filtrate was colorless. Yield 7.0 g (74%). Recrystallizations from alcohol gave slender colorless needles with constant m.p. 162-164°. Its mixed melting point with product (VII) was 158-160°.

Found %: N 9.25; S 20.41; Cl 7.63. $C_{17}H_{15}O_5N_3ClS_3$. Calculated %: N 8.90; S 20.48; Cl 7.51.

4) 2-(Benzenesulfonimido)-3-(acetylsulfanilyl-4-thiazoline (X). The product was obtained by the above

method from 2-(benzenesulfonamido)thiazole (3.7 g) and acetylsulfanilyl chloride (3.6 g). Yield of disulfamide 6.0 g (89%), m.p. 133-137°; after two recrystallizations from alcohol the weight was 3.[illegible] g ([illegible]2%), needles with m.p. 143-145°. Difficultly soluble in ether and benzene, and quite readily soluble in alcohol, acetone and pyridine.

Found %: N 9.39, 9.30. $C_{17}H_{15}O_5N_3S_3$. Calculated %: N 9.60.

5) 2-(Acetylsulfanilylimido)-3-(benzenesulfanilyl)-4-thiazoline (XI). By the above method 5.9 g of the acetylsulfothiazole and 3.5 g of benzenesulfonyl chloride gave 6.7 g (70.7%) of the disulfamide. Recrystallization from alcohol gave 5.5 g (58%) of the product; slender rods with m.p. 155-157°. Its mixture with product (IX) melted at 136-138°.

Found %: N 9.49, 9.48. $C_{17}H_{15}O_5N_3S_3$. Calculated %: N 9.60.

6) Ammonolysis of Disulfamides. a) 0.45 g of compound (VIII) was mixed in a thick-walled test tube with 1.1 ml of 15% ammonia solution. The test tube was stoppered tightly and heated on the water bath at 70° for 4 hours. The test tube was opened after cooling; its contents were transferred to a porcelain dish and evaporated to dryness. With heating the residue dissolved in soda solution (~6%). After cooling, the soda-insoluble portion was filtered and washed on the filter. Yield of dry product 0.16 g (87.7%), m.p. 141-142°. Its mixture with synthetic p-chlorobenzenesulfamide melted at 142-143°. The soda filtrate was acidified with acetic acid, the resulting precipitate filtered, washed, and dried to constant weight. Yield 0.26 g (91.6%), m.p. 255-257°. Its mixed melting point with the authentic acetylsulfothiazole was not depressed.

b) The ammonolysis of compound (IX) was run the same as described in "a". Here we obtained: 1) 63% of acetylsulfanilamide, m.p. 213° (from water), and 2) 94.5% of 2-(p-chlorobenzenesulfamido)thiazole, m.p. 198°. The mixed melting point with the synthetic product was not depressed.

c) The ammonolysis of compound (X) gave: 1) 79% of acetylsulfanilamide. m.p. 208-210°. After recrystallization from water, m.p. 212-213°. Its mixed melting point with the synthetic acetylsulfanilamide showed no depression. 2) 91.5% of 2-(benzenesulfonamido)thiazole with m.p. 168°. Its mixture with the synthetic specimen melted at 168-170°.

d) The ammonolysis of compound (XI) gave: 1) 65.5% of benzenesulfonamide with m.p. 151°, and after recrystallization from water, m.p. 152-153°. Its mixture with the product of authentic structure (m.p. 152-153°) melted at 152-153°. 2) 90.7% of the acetylsulfothiazole with m.p. 256-257°. Its mixture with the synthetic specimen melted at the same temperature.

SUMMARY

1. The alternate introduction of 2 different sulfanyl radicals in 2-aminothiazole gave isomeric disulfamides.

2. On the basis of the ammonolysis results and a study of the absorption spectra in the ultraviolet it was established that the obtained disulfamides have the thiazoline structure (VIII, IX and X, XI) (Scheme 6), and not the thiazole structure (VII) (Scheme 5).

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Ural Polytechnical Institute

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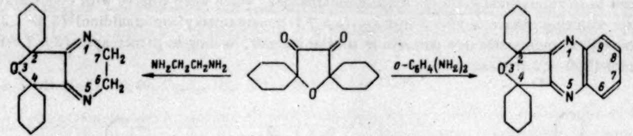
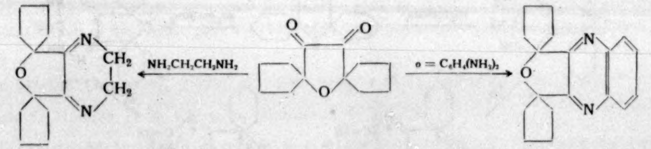
3,4-DIKETONES OF THE FURANIDINE SERIES OF THE BISPYRAN TYPE IN THE SYNTHESIS OF CONDENSED HETEROCYCLIC SYSTEMS

I. K. Korobitsyna, Yu. K. Yuryev, Yu. A. Cheburkov and E. M. Lukina

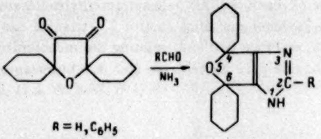
In a previous study we had shown that the 3,4-diketones of the furanidine series (2,2,5,5,-tetramethylfuranidin-3,4-dione and 2,5-dimethyl-2,5-diethylfuranidin-3,4-dione) are convenient starting substances for the synthesis of condensed heterocyclic systems, into whose composition enter the furanidine, quinoxaline, dihydropyrazine or imidazole cycles [1].

In this work we studied the reaction of the bispyran type of 3,4-diketones of the furanidine series: 2,2,5,5-bispentamethylenefuranidin-3,4-dione and 2,2,5,5-bistetramethylenefuranidin-3,4-dione [2]. Their reaction with o-phenylenediamine gave: (2,2,4,4-bispentamethylenefuranidino)-(3,4)-quinoxaline, and correspondingly, (2,2,-4,4-bistetramethylenefuranidino)-(3,4)-quinoxaline. When reacted with ethylenediamine they gave (2,2,4,4-bispentamethylenefuranidino)-(3,4)-dihydropyrazine, and correspondingly, (2,2,4,4-bistetramethylenefuranidino)-(3,4)-dihydropyrazine. In all cases the yields of reaction products were 80-90%.

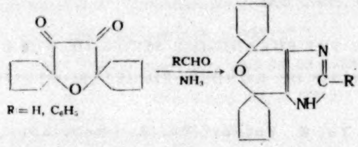




The bispyran type of 3,4-diketones also readily enter into the Radziszewski reaction [3] (with aldehydes and ammonia), giving the corresponding imidazoles. Thus, the reaction of 2,2,5,5-bispentamethylenefuranidin-3,4-dione with urotropine or benzaldehyde and ammonia gave (4,4,6,6-bispentamethylenefuranidino)-(3,4)-imidazole, and correspondingly, 2-phenyl-(4,4,6,6-bispentamethylenefuranidino)-(3,4)-imidazole:



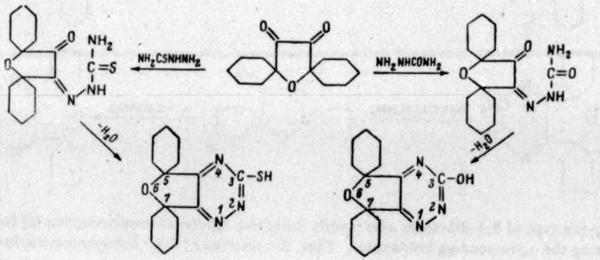
In a similar manner from 2,2,5,5-bistetramethylenefuranidin-3,4-dione we obtained (4,4,6,6-bistetramethylenefuranidino)-(3,4)-imidazole, and correspondingly, 2-phenyl-(4,4,6,6-bistetramethylenefuranidino)-(3,4)-imidazole:



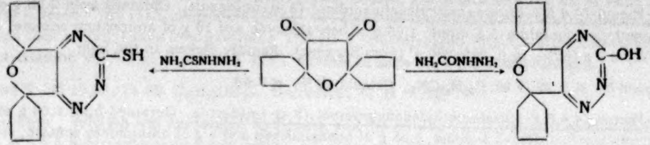
The yields of the imidazoles were 60-95%. The imidazoles, containing phenyl radicals, rapidly darkened in the light.

From the literature it is known that the reaction of α-diketones with semicarbazide can lead, depending on the reaction conditons and ratio of reagents, to the monosemicarbazone, the disemicarbazone, and to the 1,2,4-triazine cycle [4]. According to the data of Biltz [5], the reaction of equimolar amounts of semicarbazide and α-diketone gives the diketone monosemicarbazone, which when treated with alkali suffers ring closure with the formation of a 3-hydroxy-1,2,4-triazine. In a similar manner the reaction with thiosemicarbazide gives the 3-mercapto-1,2,4-triazines. In recent years this method was used to prepare a number of mercapto- and hydroxy-1,2,4-triazines [6].

In this study it was shown that the heating of 2,2,5,5-bispentamethylenefuranidin-3,4-dione with an equimolar amount of semicarbazide gives the monosemicarbazone, which when treated with concentrated alkali cleaves water with ring closure to give 3-hydroxy-(5,5,7,7-bispentamethylenefuranidino)-(3,4)-1,2,4-triazine. The reaction with thiosemicarbazide proceeds in similar manner, leading to 3-mercapto-(5,5,7,7-bispentamethylenefuranidino)-(3,4)-1,2,4-triazine.



It was shown on the example of reacting 2,2,5,5-bistetramethylenefuranidin-3,4-dione with semicarbazide that 3-hydroxy-(5,5,7,7-bistetramethylenefuranidino)-(3,4)-1,2,4-triazine can be obtained in 65% yield by reacting first with the semicarbazide, and then (without isolating the monosemicarbazone) with sodium hydroxide. Similar reaction with thiosemicarbazide gave 3-mercapto-(5,5,7,7-bistetramethylenefuranidino)-(3,4)-1,2,4-triazine:



EXPERIMENTAL

1. Preparation of Quinoxalines from 3,4-Diketones of the Furanidine Series

(2,2,4,4-Bispentamethylenefuranidino)-(3,4)-quinoxaline. A mixture of 0.6 g of 2,2,5,5-bispentamethylfuranidin-3,4-dione and 0.27 g of o-phenylenediamine was heated for 15 minutes. After dissolving in hot alcohol and adding water we obtained 0.6 g (80%) of (2,2,4,4-bispentamethylenefuranidino)-(3,4)-quinoxaline; m.p. 117.2-117.5°. Readily soluble in alcohol and pyridine.

Found %: N 9.24, 9.05. $C_{20}H_{24}ON_2$. Calculated %: N 9.08.

(2,2,4,4-Bistetramethylenefuranidino)-(3,4)-quinoxaline. Obtained, as described above, from 0.83 g of of 2,2,4,4-bistetramethylenefuranidin-3,4-dione and 0.43 g of o-phenylenediamine; m.p. 105.5-106°. Yield 1 g (90%).

Found %: N 9.99, 10.03. $C_{18}H_{20}ON_2$. Calculated %: N 10.00.

2. Preparation of Dihydropyrazines From 3,4-Diketones of the Furanidine Series

(2,2,4,4-Bispentamethylenefuranidino)-(3,4)-6,7-dihydropyrazine. Self-heating was observed when 0.6 g of 2,2,5,5-bispentamethylenefuranidin-3,4-dione was reacted with 0.19 g of ethylenediamine monohydrate. Then the mixture was heated several minutes and dissolved in 20 ml of alcohol. The addition of water gave 0.6 g (92%) of (2,2,4,4-bispentamethylenefuranidino)-(3,4)-6,7-dihydropyrazine; m.p. 64°. Readily soluble in alcohol, acetone and pyridine.

Found %: N 10.61, 10.46. $C_{16}H_{24}ON_2$. Calculated %: N 10.77.

(2,2,4,4-Bistetramethylenefuranidino)-(3,4)-6,7-dihydropyrazine. Here also the reaction of 4.16 g of 2,2,5,5-bistetramethylenefuranidin-3,4-dione with 1.6 g of ethylenediamine monohydrate was with self-heating. The reaction mixture was diluted with ether and dried over potash. Removal of the ether by distillation of 2 vacuum-distillations of the residue gave 4 g (79%) of (2,2,4,4-bistetramethylenefuranidino)-(3,4)-6,7-dihydropyrazine.

B.p. 147-148° (7 mm), n_D^{20} 1.5253, d_4^{20} 1.0900, MR_D 71.48. $C_{16}H_{20}ON_2F_2$ Calc. 71.91.

Found %: N 10.99, 11.25. $C_{14}H_{20}ON_2$. Calculated %: N 10.93.

3. Preparation of Imidazoles From 3,4-Diketones of the Furanidine Series

(4,4,6,6-Bispentamethylenefuranidino)-(3,4)-Imidazole. A mixture of 11.8 g of 2,2,5,5-bispentamethylenefuranidin 3,4-dione, 1.4 g of urotropine and 25 g of ammonium acetate was dissolved in 100 ml of glacial acetic acid and the solution heated for 2 hours in a flask under reflux. The mixture after cooling was poured into 100 ml of water, filtered, and with ice-cooling was saturated with gaseous ammonia. The resulting precipitate was suction-filtered and washed with water.

The yield of (4,4,6,6-bispentamethylenefuranidino)-(3,4)-imidazole was 10 g (81%); m.p. 213-213.5° (from benzene); readily soluble in alcohol, pyridine, chloroform and dichloroethane, and difficultly soluble in water and ether.

Found %: C 73.22, 73.20; H 8.94, 9.03; N 11.12, 11.24. $C_{15}H_{22}ON_2$. Calculated %: C 73.21; H 8.90; N 11.38.

(4,4,6,6-Bistetramethylenefuranidino)-(3,4)-imidazole. Obtained from 3 g of 2,2,5,5-bistetramethylenefuranidin-3,4-dione, 0.4 g of urotropine and 9 g of ammonium acetate by the method given above. Yield 2.8 g

(83%); m.p. 244.5-245.5° (from dichloroethane); readily soluble in alcohol, chloroform, pyridine and dioxane.

Found %: N 12.56, 12.77. $C_{13}H_{18}ON_2$. Calculated %: N 12.84.

2-Phenyl-(4,4,6,6-bispentamethylenefuranidino)-(3,4)-imidazole. Obtained from 2.36 g of 2,2,5,5-bispentamethylenefuranidin-3,4-dione, 1.06 g of benzaldehyde and 10 g of ammonium acetate, as described above. Yield 2 g (62%); m.p. 230-230.5° (from benzene). Rapidly darkens in the light.

Found %: N 9.26, 9.20. $C_{21}H_{27}ON_2$. Calculated %: N 8.69.

2-Phenyl-(4,4,6,6-bistetramethylenefuranidino)-(3,4)-imidazole. Obtained from 1.04 g of 2,2,5,5-bistetramethylenefuranidin-3,4-dione, 0.55 g of benzaldehyde and 5 g of ammonium acetate, as described above. Yield 1.4 g (95%); m.p. 204.5-205.5° (from dilute alcohol). Rapidly darkens in the light.

Found %: N 9.98, 10.11. $C_{19}H_{22}ON_2$. Calculated %: N 9.51.

4. Preparation of Hydroxy- and Mercaptotriazines From 3,4-Diketones of the Furanidine Series

3-Hydroxy-(5,5,7,7-bispentamethylenefuranidino)-(3,4)-1,2,4,-triazine. A mixture of 1.18 g of 2,2,5,5-bispentamethylenefuranidin-3,4-dione, 0.56 g of semicarbazide hydrochloride and 10 ml of glacial acetic acid was heated for 1 hour in a flask under reflux and then poured into 100 ml of water. Yield of 2,2,5,5-bispentamethylenefuranidin-3,4-dione monosemicarbazone 1.4 g (96%); m.p. 182.5-183.5° (from gasoline).

Found %: C 61.46, 61.51; H 8.01, 7.93; N 14.73, 14.82. $C_{15}H_{23}O_3N_3$. Calculated %: C 61.27; H 7.90; N 14.33.

A mixture of 0.5 g of 2,2,5,5-bispentamethylenefuranidin-3,4-dione monosemicarbazone and 10 ml of 40% sodium hydroxide was boiled for 3 hours in a flask under reflux. The solution after cooling was made slightly acid with acetic acid, the precipitate was filtered, air-dried, and recrystallized from gasoline. The yield of 3-hydroxy-(5,5,7,7-bispentamethylenefuranidino)-(3,4)-1,2,4-triazine was 0.35 g (75%); m.p. 214°. Soluble in alcohol, dioxane and acetone, and insoluble in water.

Found %: N 15.33, 15.41. $C_{15}H_{21}O_2N_3$. Calculated %: N 15.45.

3-Hydroxy-(5,5,7,7-bistetramethylenefuranidino)-(3,4)-1,2,4-triazine. A mixture of 1.04 g of 2,2,5,5-bistetramethylenefuranidin-3,4-dione, 0.56 g of semicarbazide hydrochloride and 10 ml of glacial acetic acid was boiled for 1 hour in a flask under reflux. To the cooled solution was added 20 ml of 40% sodium hydroxide solution, the mixture was heated another 2 hours, and then it was made weakly acid with acetic acid. The precipitate was filtered, dried, and recrystallized from gasoline. The yield of 3-hydroxy-(5,5,7,7-bistetramethylenefuranidino)-(3,4)-1,2,4-triazine was 0.8 g (65%); m.p. 194.5-195°. Readily soluble in acetone and alcohol; insoluble in water.

Found %: N 16.67, 16.69. $C_{13}H_{17}O_2N_3$. Calculated %: N 16.98.

3-Mercapto-(5,5,7,7-bistetramethylenefuranidino)-(3,4)-1,2,4-triazine. a) To 1.3 g of 2,2,5,5-bistetramethylenefuranidin-3,4-dione in 6 ml of pyridine was added 0.85 g of thiosemicarbazide hydrochloride in 3 ml of water. The precipitate was filtered, washed with water, and dried. The yield of 2,2,5,5-bistetramethylenefuranidin-3,4-dione monothiosemicarbazone was 1.6 g (85%); m.p. 150-151° (from dilute alcohol). Soluble in alcohol; insoluble in water.

Found %: N 13.60, 13.83. $C_{13}H_{19}O_2N_3S \cdot H_2O$. Calculated %: N 14.02.

b) A mixture of 1.04 g of 2,2,5,5-bistetramethylenefuranidin-3,4-dione, 0.56 g of thiosemicarbazide hydrochloride and 10 ml of glacial acetic acid was boiled in a flask under reflux for 1 hour. The cooled solution was treated with 20 ml of 40% sodium hydroxide solution, the mixture heated another 2 hours, and then acidified with acetic acid. The precipitate was filtered and recrystallized from gasoline. The yield of 3-mercapto-(5,5,7,7-bistetramethylenefuranidino)-(3,4)-1,2,4-triazine was 1 g (76%); m.p. 194.5-195°. Readily soluble in alcohol and acetone; insoluble in water.

Found %: C 59.87, 59.68; H 6.33, 6.65. $C_{13}H_{17}ON_3S$. Calculated %: C 59.27; H 6.46.

3-Mercapto-(5,5,7,7-bispentamethylenefuranidino)-(3,4)-1,2,4-triazine. a) A mixture of 2.36 g of 2,2,5,5-bispentamethylenefuranidin-3,4-dione, 1.27 g of thiosemicarbazide hydrochloride and 15 ml of glacial acetic acid was boiled for 1 hour in a flask under reflux, cooled, and poured into 100 ml of water. The precipitate was filtered. The reaction product (2.5 g) was dissolved in gasoline at 20°, the insoluble portion was filtered, and then recrystallized from gasoline. The yield of 3-mercapto-(5,5,7,7-bispentamethylenefuranidino)-(3,4)-1,2,4-triazine was 0.3 g; m.p. 210.5-211°. Soluble in acetone, alcohol and dioxane.

Found %: N 15.56, 15.48. $C_{15}H_{21}ON_3S$. Calculated %: N 15.72.

Gasoline solution was evaporated to dryness, and the residue was recrystallized from aqueous dioxane. The yield of 2,2,5,5-bispentamethylenefuranidin-3,4-dione monothiosemicarbazone was 0.8 g; m.p. 132-133°.

Found %: N 13.88, 13.90. $C_{15}H_{23}O_2N_3S$. Calculated %: N 13.62.

b) A mixture of 0.25 g of 2,2,5,5-bispentamethylelefuranidin-3,4-dione monothiosemicarbazone and 7.5 ml of 40% sodium hydroxide solution was boiled for 2 hours in a flask under reflux. The solution after cooling was made weakly acid with acetic acid; the precipitate was filtered and then recrystallized from gasoline. The yield of 3-mercapto-(5,5,7,7-bispentamethylenefuranidino)-(3,4)-1,2,4-triazine was 0.2 g; m.p. 210-211°. The melting point of its mixture with the substance obtained in the preceding experiment (m.p. 210.5-211°) failed to be depressed; m.p. 209-210°.

SUMMARY

1. The bispyran type of 3,4-diketones of the furanidine series are convenient substances for the synthesis of condensed heterocyclic systems—quinoxalines, dihydropyrazines and imidazoles, in whose composition the furanidine ring is found.

2. The bispyran type of 3,4-diketones of the furanidine series can also be successfully used for the synthesis of 3-hydroxy- and 3-mercapto-1,2,4-triazines, containing the furanidine ring.

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Moscow State University

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*T.p. = C. B. Translation pagination.

3. [illegible] A mixture of [illegible] g of [illegible] ml of glacial acetic acid was boiled for 1 hour in a flask under reflux, cooled and poured into 500 ml of water. The precipitate was filtered. [illegible] The yield of [illegible] soluble in benzene, [illegible]

Found %: N [illegible]. Calculated %: N [illegible]

[illegible] The yield of [illegible]

Found %: N [illegible]. Calculated %: N [illegible]

4. A mixture of [illegible] was boiled for [illegible] hours in a flask under reflux. [illegible] cooling was made weakly acid with acetic acid, [illegible] washing. [illegible]

SUMMARY

1. [illegible]

2. [illegible]

LITERATURE CITED

[1] [illegible]

[2] [illegible]

[3] [illegible]

[4] [illegible]

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[6] [illegible]

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* See C. B. Translation pagination.

ACONITE ALKALOIDS

VIII. IDENTITY OF DELPHELATINE WITH ELDELINE

A. D. Kuzovkov

The alkaloid delphelatine $C_{30}H_{47}O_9N$ was isolated by V. V. Feofilaktov and L. D. Alekseeva from the plant Delphiniumelatum, collected by P. S. Massagetov in the Altai mountains. Together with M. S. Rabinovich we had communicated earlier [2] on the isolation of the alkaloid eldeline $C_{27}H_{41}O_8N$ from the same plant specimen.

V. V. Feofilaktov and L. D Alekseeva [1] compared the constants of their isolated alkaloid, its salts and the amino alcohol obtained on saponification, with the constants of eldeline, the corresponding salts and the amino alcohol eldelidine– the saponification product of eldeline. The constants of all of the compared substances either coincide or are close to each other. The decision of the authors that delphelatine and eldeline are different is based on the difference in the composition of these substances, and on the absence of a methylenedioxy group in delphelatine, which is present in eldeline.

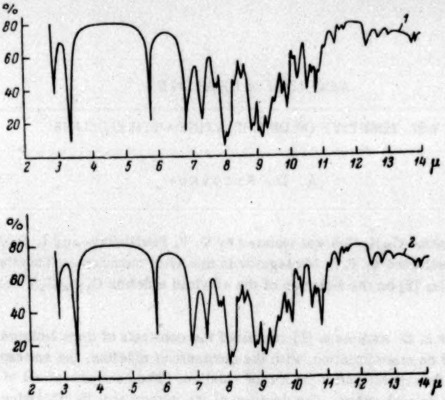
Recently we obtained from L. D Alekseeva a specimen of delphelatine hydrochloride with m.p. 214-215°. For comparison from an eldeline specimen (m.p. 183-185°), isolated earlier by M. S. Rabinovich, the hydrochloride with m.p. 216-216.5° (from a mixture of anhydrous alcohol and absolute ether) was prepared. The mixture of the two specimens melted at 215-215.5°. Both hydrochlorides have the same infrared absorption spectra (see Figure). Both substances gave a positive reaction when qualitatively tested for the presence of a methylenedioxy group by the Clowes-Tollens method [3].

The data obtained by us show that delphelatine and eldeline are the same substance, for which the name eldeline can be retained in the future.

The empirical formula, proposed by M. S. Rabinovich [2] for eldeline, is in better agreement with the determination results for the composition of the alkaloid than is the formula proposed for delphelatine. The analyses of the alkaloid and of its salts for the C, H, N and OCH_3 content [1,2] correspond equally well to both formulas. Different results were obtained when the OH content was determined: V. V. Feofilaktov and L. D. Alekseeva postulate the presence of two hydroxyl groups in the alkaloid, while the data of M. S. Rabinovich indicate the presence of only one hydroxyl. We confirmed the presence of only one hydroxyl group when we analyzed eldeline (found %: OH 3.60; calculated %: OH 3.35).

A recently published communication by Edwards and his coworkers [4] on the pinacolin rearrangement, observed in the treatment of lycoctonine with strong acids, causes us to communicate on the observations that we made in studying eldelidine. The heating of eldelidine with dilute hydrochloric acid (1:1) at 80-90° in the presence of phloroglucinol resulted in saponification of the methylenedioxy group. The reaction product, for which we propose the name demethylene eldelidine, has the composition $C_{24}H_{39}O_7N$, contains one glycol group (1.2 moles of oxidizing agent is consumed when oxidized with periodic acid), and fails to contain any carbonyl groups (absence of the corresponding band in the infrared absorption spectrum). The boiling of demethyleneeldelidine with concentrated hydriodic acid gave a crystalline oxo compound of composition $C_{21}H_{31}O_4N$; its infrared spectrum shows bands at 3565 cm^{-1} (OH) and 1725 cm^{-1} (keto group in a six-membered ring). The base forms well crystallizing salts. Our explanation for the formation of the oxo compound is that the demethyleneeldelidine, containing a glycol group, suffers pinacolin rearrangement under the influence of hydriodic acid.

A hydrocarbon is obtained when the oxo compound is dehydrogenated with selenium, giving a crystalline trinitrobenzene derivative with m.p. 100-102°, and apparently being a polycyclic aromatic hydrocarbon. We were unable to obtain any aromatic hydrocarbons when eldelidine was subjected to similar dehydrogenation.



Infrared absorption spectra in vaseline oil of the hydrochlorides of eldeline and delphelatine. 1) eldeline hydrochloride, 2) delphelatine hydrochloride.

EXPERIMENTAL

Demethyleneeldelidine. A mixture of 80 g of eldelidine and 40 g of phloroglucinol was dissolved in 4 liters of hydrochloric acid (1:1) and heated for 2 hours at 80-90°. Further treatment was by the method described earlier [5]. The yield of phloroglucide was 31 g, which corresponds to a content of one methylenedioxy group (found %: CH_2 3.9; calculated %: CH_2 3.4). Here the base was isolated (yield 47 g), which after drying at 80° had m.p. 106-108° (from aqueous acetone) and $[\alpha]_D$ + 32.0° (c = 2.0; alcohol).

The Hydrochloride was obtained in the usual manner; m.p. 230-231° (with decomp.) (from a mixture of alcohol and ether) and $[\alpha]_D$ + 7.94° (c = 2.0; alcohol).

Found %: C 57.77; H 8.31; Cl 6.98. $C_{24}H_{39}O_7N \cdot HCl \cdot 0.5\ H_2O$. Calculated %: C 57.77; H 8.28; Cl 7.11.

The Hydrobromide was obtained by adding concentrated hydrobromic acid to an acetone solution of the base. The salt melted with decomposition at 198-199° (from a mixture of alcohol and ether).

Found %: Br 15.10. $C_{24}H_{39}O_7N \cdot HBr$. Calculated %: Br 14.98.

Oxo Compound. A mixture of 47 g of demethyleneeldelidine, 470 ml of concentrated HI and 12 g of red phosphorus was heated with descending condenser until most of the methyl iodide had distilled (9 g; b.p. 43°). After this the mixture was boiled for 6 hours under reflux, adding in portions during this time 15 g of red phosphorus. The hot solution was filtered through a glass filter; the hydriodic acid was distilled from the filtrate in vacuo. Then the residue was treated with 470 ml of HCl (1:1) and 23 g of granulated zinc, and the whole was boiled under reflux for 5 hours, during which time another 23 g of zinc was added. The solution was cooled, separated from tarry substances and zinc, and made alkaline under cooling with aqueous ammonia. The base was extracted with ether. The yield of yellow oily base was 30 g. It was dissolved in 50 ml of acetone, and the solution made acid with concd. HBr. The crystalline hydrobromide precipitated immediately; yield 17 g. Recrystallization from water gave 8 g of the hydrobromide with m.p. 274-276°.

Found %: C 57.11; H 7.54; Br 17.99; N 3.12. $C_{21}H_{31}O_4N \cdot HBr$. Calculated %: C 57.01; H 7.29; Br 18.06; N 3.17.

The base was obtained from the hydrobromide in the usual manner, which after recrystallization from aqueous alcohol and then from benzene had m.p. 207-208.5° and $[\alpha]_D$ + 53.8° (c = 2.0; alcohol).

Found %: N 4.03. M 410. $C_{21}H_{31}O_4N$. Calculated %: N 3.87. M 361.

Dehydrogenation With Selenium. A mixture of 5 g of demethyleneeldelidine and 5 g of selenium was heated at 320-340° for 8 hours. The reaction products were extracted with ether, and the extract was washed successively with 10% H_2SO_4, 10% NaOH solution and water, and then evaporated. Here we obtained 1 g of tarry brown substance, the solution of which in 15 ml of petroleum ether was chromatographed on 50 g of Al_2O_3. Petroleum ether was used for the elution. The eluate of the top half of the zone, showing fluorescence in ultraviolet light, gave 100 mg of yellow oil, from which the trinitrobenzene derivative was prepared; yield 45 mg; m.p. 100-102° (from alcohol).

SUMMARY

1. The identity of delphelatine with eldeline was established.

2. Demethyleneeldelidine was obtained.

3. Experiments were run on the cleavage of demethyleneeldelidine with concentrated hydriodic acid and red phosphorus, and also on its dehydrogenation with selenium.

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S. Ordzhonikidze All-Union
Scientific-Research Institute
of Pharmaceutical Chemistry

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* T. p. = C. B. Translation pagination.

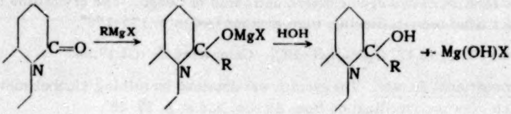
STUDY OF C_{15} ALKALOIDS

I. SOPHOCARPINOLS

A. S. Sadykov, O. S. Otroshchenko and Yu. K. Kushmuradov

In the study of N. F. Proskurnina and A. D. Kuzovkov [1] it was shown that sophocarpine has a matrine skeleton but differs from it by the presence of a double bond. However, the behavior of these alkaloids toward alkalies does not permit making a final decision as to the identity of their skeletons. Thus, for example, the treatment of matrine with potassium hydroxide yields matrinic acid due to cleavage of the lactam ring in the alkaloid; sophocarpine fails to change when treated with alkalies. Proceeding from this, and also from the fact that sophocarpine is an industrial waste, we began a study of this alkaloid.

In this paper we communicate the results obtained by us in studying the reaction of sophocarpine with organomagnesium compounds, in accord with the scheme:



Winterfeld and Petkow [2] were the first to run a similar reaction with lupanine. The authors were able to study the reaction conditions, isolate the alkyllupanols, and in this way demonstrate the possibility of introducing alkyl groups into lupanine.

The wastes from the production of pachycarpine from the heavy-bearing sophora served as the source of the sophocarpine used in our study.

The reaction of sophocarpine with organomagnesium compounds was carried out under the usual conditions of adding an ether solution of sophocarpine to the Grignard reagent. The reactions were run with C_6H_5MgBr and C_2H_5MgI. The phenylsophocarpinol was isolated from the reaction mixture as the hydriodide, obtained with the aid of ammonium iodide. This shows that the introduction of a hydroxyl group increases the basic properties of sophocarpine, since sophocarpine itself fails to react with ammonium iodide [3].

Phenylsophocarpinol is a crystalline substance with m.p. 69°; it gives a hydriodide with m.p. 150-151°; the hydrochloride with m.p. 175-176°; the picrate with m.p. 97-98°; and the hydrochloride of the acetyl derivative with m.p. 225-226°.

Ethylsophocarpinol appears as colorless crystals with m.p. 98-99°; it gives a hydriodide with m.p. 309-310° and a picrate with m.p. 224-225°.

Determination of active hydrogen by the Terentyev and Kupletskaya procedure [4] revealed the presence of one hydroxyl group in the alcohols. Treatment with acetyl chloride gave the corresponding acetyl derivatives as the hydrochlorides. The hydrochloride of the acetyl derivative of ethylsophocarpinol is extremely hygroscopic; it retains its crystalline structure only in solvents (in ether).

EXPERIMENTAL

Isolation of Sophocarpine. A sample of 250 g of high-boiling bases from the heavy-bearing sophora (plant wastes) was separated into three fractions by vacuum-distillation: 1st fraction, b.p. 150-170° (5 mm), 3 g (1.2%) of pachycarpine; 2nd fraction, b.p. 170-210° (5 mm), 55 g (22%) of sophocarpine; residue, 192 g (76.8%) of sophoramine and others. The sophocarpine was characterized as the hydriodide (m.p. 276°), the hydrochloride (m.p. 305-306°), and the picrate (m.p. 120-121°).

Phenylsophocarpinol. To an ether solution of phenylmagnesium bromide, obtained from 4.5 g of Mg, 350 ml of absolute ether and 30 g of bromobenzene, was added with cooling an ether solution of 45 g of anhydrous freshly distilled sophocarpine. Then the reaction mixture was heated for 2 hours. The reaction product after cooling was decomposed with 10% hydrochloric acid. The acid solution was washed several times with ether (to remove unreacted bromobenzene), then made alkaline with 23% ammonia, and after saturation with potash was then extracted with ether. The ether extract was dried over fused potash, and the ether removed by distillation. The residue (50 g) was dissolved in 300 ml of acetone and the resulting solution was treated with an acetone solution of 29 g of ammonium iodide. On shaking ammonia was evolved and the phenylsophocarpinol hydriodide deposited as a crystalline precipitate. Recrystallization from alcohol gave 35 g (59.3%) of the hydriodide with m.p. 150-151°. The hydriodide is readily soluble in water and alcohol, and difficultly soluble in anhydrous alcohol.

Found %: I 27.8, 28.3; N 6.64, 7.00. $C_{21}H_{28}N_2O \cdot HI$. Calculated %: I 28.0; N 6.19.

To an aqueous solution of 10 g of phenylsophocarpinol hydriodide was added with heating a 30% sodium hydroxide solution. The oil that separated here was extracted with ether. After drying and distilling off the solvent the phenylsophocarpinol was obtained as a crystalline substance with m.p. 69° (from aqueous alcohol 1:3).

Found: $H_{act.}$ 1.006, 1.008. $C_{21}H_{28}ON_2$. Calculated: $H_{act.}$ 1.00.

Phenylsophocarpinol Hydrochloride. To 2 g of phenylsophocarpinol in 25 ml of acetone was added in drops an acetone solution of hydrogen chloride until acid to Congo. The crystalline hydrochloride deposited on standing, which after recrystallization from acetone had m.p. 175-176°.

Found %: Cl 17.19, 18.12. $C_{21}H_{28}N_2O \cdot HCl$. Calculated %: Cl 17.88.

Phenylsophocarpinol Picrate. The picrate was obtained by mixing alcohol solutions of the base and picric acid, which after recrystallization from alcohol had m.p. 97-98°.

Hydrochloride of the Acetyl Derivative of Phenylsophocarpinol. To a cooled solution of 10 g of the base in 30 ml of ether was added acetyl chloride in drops. The resulting white resinous precipitate was washed several times by decantation with hot acetone. After recrystallization from acetone the hydrochloride had m.p. 225-226°.

Found %: Cl 7.38, 6.37, 6.37. $C_{21}H_{27}OCOCH_3 \cdot HCl$. Calculated %: Cl 6.9.

Ethylsophocarpinol. To an ether solution of ethylmagnesium iodide, prepared from 8 g of Mg, 400 ml of absolute ether and 60 g of ethyl iodide, was gradually added with cooling and stirring an ether solution of 88 g of freshly distilled sophocarpine. Then the mixture was heated for 2 hours on the water bath. Further treatment and isolation of the reaction product were the same as for the phenylsophocarpinol. The yield of ethylsophocarpinol with m.p. 98-99° (from methyl alcohol) was 20 g (21%).

Found : $H_{act.}$ 1.09, 1.20. $C_{17}H_{28}ON_2$. Calculated: $H_{act.}$ 1.00.

Ethylsophocarpinol Hydriodide. To 2 g of ethylsophocarpinol in 20 ml of acetone was added 1.8 g of ammonium iodide. Shaking of the mixture resulted in ammonia evolution and the deposition of the hydriodide as a crystalline precipitate with m.p. 309-310° (from alcohol).

Ethylsophocarpinol Hydrochloride is obtained as a precipitate when acetone solutions of the base and hydrochloric acid are mixed. We were unable ot determine the melting point of the compound due to its extreme hygroscopicity.

Ethylsophocarpinol Picrate. Obtained by mixing alcohol solutions of the base and picric acid. After recrystallization from alcohol, m.p. 224-225°.

SUMMARY

1. The lactam group of sophocarpine was reacted with organomagnesium compounds. Two new alcohols were obtained: phenylsophocarpinol and ethylsophocarpinol, which were characterized by preparing some of the salts and derivatives.

2. Ammonium iodide was used for the first time to isolate the products from the reaction mixture as hydriodides.

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*T.p. = C. B. Translation pagination.

ALKALOIDS OF THE BRANCHY PLANTAIN (PLANTAGO RAMOSA, SYN. P. INDICA), II

A. V. Danilova

Earlier we had communicated on the isolation of three alkaloids from the plantain – plantagonine ($C_{10}H_{11}O_2N$), indicamine ($C_{14}H_{23}ON$) and indicaine (II) ($C_{10}H_{11}ON$) [1]. In this paper we communicate on the functions of the oxygen atoms in plantagonine and indicaine and on the interrelationships of these two alkaloids.

The work was done with the plantain that had been extracted from the seeds of the Caucasian plant at the Chimkent Experimental Station of VILAR;* here it was established that the plantain, collected in the rosette stage, contains only 0.02% total alkaloids, from which individual substances could not be isolated. The plantain, collected in the flowering stage, contains about 0.2% total alkaloid bases. The purification and separation of this mixture revealed that it is mainly composed of resinous substances and the alkaloid indicaine.

Indicaine fails to form a nitroso derivative with sodium nitrite solution, which indicates the tertiary nature of the nitrogen. When oxidized with either nitric acid or silver oxide the indicaine is converted to plantagonine. With ammoniacal silver solution it forms a silver mirror. With an alcoholic solution of 2,4-dinitrophenylhydrazine hydrochloride it gives the 2,4-dinitrophenylhydrazone (hydrochloride). On the basis of this information it was concluded that indicaine is an amino aldehyde. When indicaine is reduced with PtO_2 it adds 1 mole of hydrogen, forming an amino alcohol, which was characterized as the oxalate and as the picrate. Proceeding from the observations that plantagonine dissolves in organic solvents at pH 6, and also from the fact that it dissolves in sodium bicarbonate solution with the evolution of CO_2, we postulated that it is an amino acid. This was confirmed by obtaining the ethyl ester of plantagonine.

Establishing the function of the oxygen atoms in plantagonine and indicaine indicates the interrelationship of these two alkaloids.

EXPERIMENTAL

1. Extraction of Alkaloids From the Plantain in the Flowering Stage. The finely pulverized plant (15 kg) was moistened with 10% ammonia solution and the alkaloids were exhaustively extracted with dichloroethane in a percolator. The alkaloids were extracted from the dichloroethane with 10% H_2SO_4. The acid solution was filtered, treated with ammonia to pH 6, and the bases extracted first with ether, and then with chloroform. The ether extract gave 26.4 g of total bases while the chloroform solution gave 2.78 g. The total alkaloid content of the plant was 0.19%. The alkaloids from the ether are a mobile dark-brown oil without a basic odor. The alkaloids from the chloroform are a viscous, black substance.

2. Isolation of Indicaine From the Ether Extract of Total Alkaloids in a Column With Al_2O_3. The substance (0.3 g) was dissolved in ether, filtered to remove a small amount of flocculent residue, and passed through a column containing 7 g of Al_2O_3. Ether was used for the elution, collecting 10 ml fractions. A total of 6 fractions was collected, and the total weight of eluted substance was 0.29 g. Not one of the fractions gave a crystalline substance. Each fraction was dissolved in alcohol and mixed with a saturated alcohol solution of picric acid. Only the 1st and 2nd fractions gave a picrate as precipitate, a total of 0.2 g. After 2 recrystallizations from acetone the picrate melted at 152-153°, weight 0.08 g (indicaine).

Then we obtained the picrate without prior purification of the total alkaloids in the column, for which 26 g of total bases was dissolved in ethyl acetate and filtered. The solution was treated with a saturated ethyl acetate solution of picric acid. The resulting picrate was separated from the liquid, washed with ethyl acetate, and dried. Weight of picrate 16.2 g, m.p. 127-129°. After 4 recrystallizations from acetone, m.p. 151-152°, weight 6.25 g.

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* VILAR – All-Union Institute of Curative and Aromatic Plants.

3. Isolation of the Base from Indicaine Picrate. A mixture of 3.16 g of indicaine picrate and 15 ml of 17% HCl was extracted with ether to remove the picric acid. The acid solution was made alkaline with 20% NH_4OH to pH 7 and then extracted with ether. The ether solution gave 1.19 g of indicaine as a mobile yellow liquid.

4. Catalytic Reduction of Indicaine (Dihydroindicaine). A solution of 1 g of indicaine in 15 ml of alcohol was treated with 0.1 g of PtO_2 and then reduced with hydrogen at atmospheric pressure. The amount of hydrogen absorbed in 3 hours was 160 ml (1 mole). The catalyst was filtered and the alcohol was vacuum-distilled; the dihydroindicaine was dried to constant weight in a vacuum-desiccator. A viscous colorless oil was obtained, readily soluble in alcohol, but failing to decolorize a sulfuric acid solution of potassium permanganate.

Oxalate. A solution of the base in alcohol was treated with an alcohol solution of oxalic acid. After 2 recrystallizations from alcohol the crystalline oxalate method at 120.5-121.5°.

Found %: C 63.54; H 6.50; N 6.79. $(C_{10}H_{13}ON)_2 \cdot C_2H_2O_4$. Calculated %: C 63.46; H 6.73; N 6.73.

The Picrate was obtained by mixing alcohol solutions of the base and picric acid. After 3 recrystallizations from alcohol, m.p. 147-148°.

Found %: C 48.15; H 4.01; N 14.18. $C_{10}H_{13}ON \cdot C_6H_3O_7N_3$. Calculated %: C 48.96; H 4.08; N 14.28.

5. Oxidation of Indicaine With Silver Oxide to Plantagonine. 1.4 g of indicaine was added to an ammoniacal solution of silver oxide prepared from 6 g of $AgNO_3$. The mixture was heated under reflux on the water bath for 1 hour; a silver mirror formed on the sides of the flask. The ammoniacal solution was filtered and acidified with 20% H_2SO_4 to pH 6; here a precipitate separated. The liquid was suction-filtered, and the precipitate was washed with water and dried, weight 1.2 g. The substance fails to show a sharp melting point, is insoluble in water and organic solvents, and gives a positive test for silver; it apparently is the silver salt of an amino acid. It was suspended in 50 ml of water, the mixture heated to the boil, and then treated with a stream of hydrogen sulfide. The silver sulfide precipitate was separated and washed with water. Extraction of the filtrate with ether gave 0.25 g of crystalline substance with m.p. 221-222°, failing to show a melting point depression when mixed with plantagonine.

6. Oxidation of Indicaine With Nitric Acid (Plantagonine Nitrate). A mixture of 1.54 g of indicaine and 15 ml of nitric acid (d 1.18) was heated for 1 hour under reflux on the boiling water bath. The mixture was cooled, transferred to a separatory funnel, and the acid solution shaken with ether; here a precipitate was obtained, weight 0.78 g, m.p. 142-143°. After 3 recrystallizations from anhydrous alcohol, weight 0.33 g, m.p. 147-148°.

Found %: C 50.26; H 5.00; N 11.31. $C_{10}H_{11}O_2N \cdot HNO_3$. Calculated %: C 50.00; H 5.00; N 11.66.

Decomposition of Plantagonine Nitrate. A solution of 0.25 g of the nitrate in 1 ml of water was treated dropwise with a 10% NH_3 solution to pH 6, and the base was extracted with ether. Removal of the ether by distillation gave 0.08 g of plantagonine with m.p. 218-219°. The acid aqueous solution was made alkaline with ammonia and extracted with ether. Removal of the ether by distillation gave 0.053 g of liquid, being unchanged indicaine (based on the melting point of the picrate and the formation of a silver solution). The aqueous solution was neutralized to pH 7, condensed to a volume of 2 ml, and extracted with ether. Removal of the ether by distillation gave 0.02 g of substance with m.p. 217-218°, failing to show a melting point depression when mixed with plantagonine.

7. Ethyl Ester of Plantagonine. A mixture of 0.35 g of plantagonine and 10 ml of an alcoholic hydrochloric acid solution (15%) was heated under reflux for 1 hour. The mixture was poured into water, neutralized with sodium bicarbonate, and extracted with ether. From the ether was obtained 0.38 g of noncrystalline substance. Vacuum-distillation (0.5 mm) with heating on the boiling water bath gave a colorless substance with m.p. 43-45° $[\alpha]_D + 29.4°$ (c = 4; alcohol).

Found %: C 70.12; H 7.21; N 6.79. $C_{12}H_{15}O_2N$. Calculated %: C 70.24; H 7.31; N 6.83.

SUMMARY

1. It was established that plantagonine is an amino acid. The ethyl ester of plantagonine was prepared.

2. It was established that indicaine is an amino aldehyde. Reduction of indicaine in the presence of platinum oxide gives an amino alcohol (dihydroindicaine), which was characterized as the picrate and as the oxalate.

3. The oxidation of indicaine with either silver oxide or nitric acid yields plantagonine. In this way the interrelationship between the two alkaloids of the plantain—plantagonine and indicaine—was established.

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S. Ordzhonikidze All-Union
Scientific-Research Chemical-Pharmaceutical
Institute

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1,2-NAPHTHO-(3',4')-FUROXAN SERIES

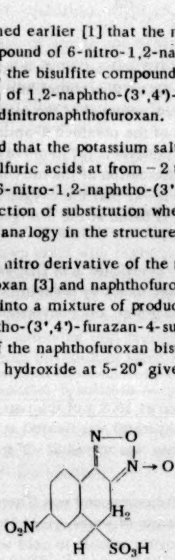
VI. THE BISULFITE COMPOUND OF 6-NITRO-1,2-NAPHTHO-(3',4')-FUROXAN AND ITS DERIVATIVES

S. V. Bogdanov and N. I. Zilberman

It has been mentioned earlier [1] that the nitration of the bisulfite compound of 1,2-naphtho-(3',4')-furazan leads to the bisulfite compound of 6-nitro-1,2-naphtho(3',4')-furazan. It also seemed of interest to elucidate the possibility of nitrating the bisulfite compound of 1,2-naphtho-(3',4')-furoxan. According to the data of Green and Rowe [2] the nitration of 1,2-naphtho-(3',4')-furoxan itself even with an equimolar amount of nitric acid gives only 4-(or 3-), 5-(or 8-)-dinitronaphthofuroxan.

Experiment revealed that the potassium salt of the naphthofuroxan bisulfite compound, when treated with a mixture of nitric and sulfuric acids at from −2 to −4°, is also transformed into a nitration product, from which the potassium salt of the 6-nitro-1,2-naphtho-(3',4')-furoxan bisulfite compound (I) was isolated in 66-70% yield. The similarity in the direction of substitution when the bisulfite compounds of naphtofurazan and naphthofuroxan are nitrated indicates the analogy in the structure of the hydrocarbon rings of these substances.

In its properties the nitro derivative of the naphthofuroxan bisulfite compound closely resembles the bisulfite compounds of naphthofuroxan [3] and naphthofuroxan-6-sulfonic acid [4]. Under short treatment with 1% potash solution it is transformed into a mixture of products, from which 2,6-dinitro-1-naphthylamine-4-sulfonic acid (II) and 6-nitro-1,2-naphtho-(3',4')-furazan-4-sulfonic acid were isolated. Here the yield of amino compound is only 32.7% (in the case of the naphthofuroxan bisulfite compound it reached 85%). Treatment of the bisulfite compound with potassium hydroxide at 5-20° gives 6-nitro-1,2-naphthoquinone-4-sulfonic acid dioxime (III) in 54% yield:



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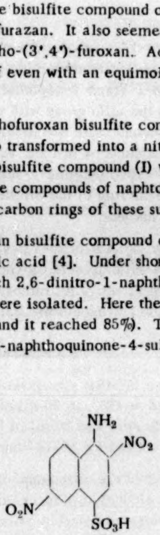
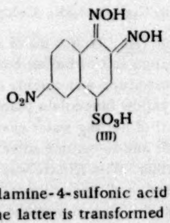
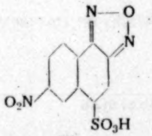


(II)

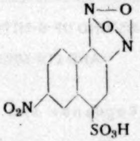


(III)

The boiling of 2,6-dinitro-1-naphthylamine-4-sulfonic acid (II) with 13% potash solution converts it into 2,6-dinitro-1-naphthol-4-sulfonic acid. The latter is transformed into 2,4,6-trinitro-1-naphthol when heated with dilute nitric acid. The heating of the dinitronaphthylaminesulfonic acid (II) with 40% sulfuric acid leads to 2,6-dinitro-1-naphthylamine. Even in acid medium the diazo compounds from 2,6-dinitro-1-naphthylamine-4-sulfonic acid (II) and from 2,6-dinitro-1-naphthylamine are, respectively, converted into 6-nitro-1-diazo-2-naphthol-4-sulfonic acid and 6-nitro-1-diazo-2-naphthol 6-Nitro-1,2-naphthoquinone-4-sulfonic acid dioxime (III) under further treatment with potassium hydroxide is converted into 6-nitro-1,2-naphtho-(3',4')-furazan-4-sulfonic acid (IV). and when oxidized with nitric acid– into 6-nitro-1,2-naphtho-(3',4')-furoxan-4-sulfonic acid (V). (A symmetrical structure for the furoxan ring was tentatively assumed in the formula). The treatment of 6-nitro-1,2-naphthofurazan-4-sulfonic acid (IV) with potassium hypochlorite and hydrochloric acid converts it into 4-chloro-6-nitro-1,2-naphthofurazan.



(IV)



(V)

The structure of 2,6-dinitro-1-naphthylamine-4-sulfonic acid (II) was established by two routes: a) its transformation through 2,6-dinitro-1-naphthylamine and 6-nitro-1-diazo-2-naphthol into 6-nitro-2-naphthol, and b) its conversion into 6-nitro-1-diazo-2-naphthol-4-sulfonic acid, removal of the diazo group, reduction of the nitro group, and cleavage of the sulfo group with transformation of the obtained 6-amino-2-naphthol into the dibenzoyl derivative. The second route was used by Ruggli and coworkers [5] to prove the structure of the nitration product of 1-diazo-2-naphthol-4-sulfonic acid. The transformation of the nitronaphthofuroxan bisulfite compound (I) into 2,6-dinitro-1-naphthylamine-4-sulfonic acid (II) shows that the oxygen atom, not being common to the nitrogen atoms in the furoxan ring of the bisulfite compound, is found at the nitrogen linked with the second carbon atom of the naphthalene nucleus.

The position of the sulfo group in 6-nitro-1,2-naphthofurazan-4-sulfonic acid (II), and consequently, also in 6-nitro-1,2-naphthoquinone-4-sulfonic acid dioxime (III), was made exact by reducing the nitrofurazansulfonic acid to the aminonaphthofurazansulfonic acid, removal of the amino group and conversion of the obtained naphthofurazansulfonic acid into 4-chloro-1,2-naphthofurazan.

EXPERIMENTAL

6-Nitro-1,2-naphthofuroxan Bisulfite Compound (I). A solution of 15.3 g of the potassium salt of the naphthofuroxan bisulfite compound, dried at 125°, in 94 ml of H_2SO_4 (monohydrate) was treated at −2° in 1 hour with a mixture of 3.32 g of 97.68% nitric acid and 20 ml of H_2SO_4. The mass was stirred at −2° to −4° for 2 hours, diluted with 280 g of ice, and allowed to stand for 12-14 hours.

The obtained potassium salt of the nitronaphthofuroxan bisulfite compound was filtered, washed with potassium acetate solution, then with alcohol, and recrystallized from 6 parts of water; yield 11.4-12.3 g, i.e., 65-70%. The potassium salt appeared elongated colorless prisms, quite difficultly soluble in cold water; it does not lose weight at 150°.

Found %: C 33.78; H 1.78; N 11.44; K 11.10. $C_{10}H_6O_7N_3SK$. Calculated %: C 34.18; H 1.72; N 11.96; K 11.13.

2,6-Dinitro-1-naphthylamine-4-sulfonic Acid (II). To 500 ml of a boiling 1% potash solution was added in 2 minutes a 50% water paste of 17.5 g of the potassium salt of the nitronaphthofuroxan bisulfite compound, and the mixture was boiled for 2 minutes. The resulting suspension was quickly cooled to 18° and the precipitate, consisting of orange rhombic plates yellow needles and yellow lanceolate plates, was filtered; the precipitate weighed 11.25 g. Treatment of the precipitate with 14 parts of boiling water gave 1.4 g of insoluble residue. It represented yellow needles, very difficultly soluble in hot water and in organic solvents. The substance contained both nitrogen and sulfur, and did not melt; it was not studied further. The filtrate was cooled to 40°, the resulting potassium salt of the dinitronaphthylaminesulfonic acid was filtered, and then recrystallized from water; yield 6.05 g (32.7%). The filtrate from the potassium salt of the dinitronaphthylaminesulfonic acid (and also the partially evaporated filtrate from its recrystallization) gave the potassium salt of 6-nitro-1,2-naphthofurazan-4-sulfonic acid; the total yield of this substance after recrystallization from water was 3.6 g (20%).

The potassium salt of the dinitronaphthylaminesulfonic acid was obtained as stout orange prisms with a rhombic base, quite difficultly soluble in cold water; after drying it assumes a red color.

Found %: H_2O 4.92 (dried at 130°); K 10.55; N 11.98 (in dry substance). $C_{10}H_6O_7N_3SK \cdot H_2O$. Calculated %: H_2O 4.88; K 10.59. $C_{10}H_6O_7N_3SK$. Calculated %: N 11.96.

O,N-Dibenzoyl-6-amino-2-naphthol. A suspension of 7.2 g of the potassium salt of the dinitronaphthylaminesulfonic acid in 40 ml of c.p. sulfuric acid was treated at 2-5° with a solution of 1.63 g of sodium nitrite in 20 ml of sulfuric acid, and the mixture was kept for 4 hours at 5-8°. The obtained diazo solution gave a red-violet color with 2-naphthol-3,6-disulfonic acid, and a brown color with resorcinol. The addition of 200 g of ice to the sulfuric acid solution gave a precipitate of 6-nitro-1-diazo-2-naphthol-4-sulfonic acid, failing to couple with 2-naphthol-3,6-disulfonic acid, and giving a deep violet color with resorcinol. The filtered diazo compound was reprecipitated from soda solution; yield 5.6 g. The further stages of obtaining the dibenzoyl derivative of 6-amino-2-naphthol were accomplished by the methods described by Ruggli and coworkers [5]. Colorless plates (from acetic acid); m.p. 233.5°. From the data of Ruggli and coworkers, m.p. 228-230°.

Found %: N 3.78 (Kjeldahl). $C_{24}H_{17}O_3N$. Calculated %: N 3.81.

2,6-Dinitro-1-naphthylamine and 6-Nitro-2-naphthol. One gram of the potassium salt of the dinitronaphthylaminesulfonic acid was heated with 30 ml of 40% sulfuric acid at 110° for 3.5 hours. The mixture was diluted with water, and the dinitronaphthylamine was filtered and washed with water and ammonia; yield 0.56 g. Red-orange tetrahedral prisms (from acetic acid), readily soluble in ether and difficultly soluble in alcohol and acetic acid, m.p. 300.2° (decompn.).

Found %: N 18.19. $C_{10}H_7O_4N_3$. Calculated %: N 18.02.

A solution of 1.16 g of the dinitronaphthylamine in 20 ml of c.p. sulfuric acid was treated at 2-5° with a solution of 0.416 g of sodium nitrite in 5 ml of sulfuric acid, the mixture kept at 2-4° for 4 hours, and then diluted with 100 g of ice. Originally the diazo compound gave an orange-red color with 2-naphthol-3,6-disulfonic acid, and a brown color with resorcinol, but after diluting the solution with ice it coupled only with resorcinol with the formation of a violet dye. The precipitated 6-nitro-1-diazo-2-naphthol was filtered and washed with water. The solution of the moist diazo compound in 25 ml of alcohol was treated with 0.1 g of cuprous oxide, and the mixture was boiled for 18 hours. After separating the copper the alcohol was distilled off, and the residue was extracted with boiling water. Pale-yellow prisms of 6-nitro-2-naphthol with m.p. 158.2-159° deposited from the aqueous solution; from the literature, m.p. 158° [6].

2,6-Dinitro-1-naphthol-4-sulfonic Acid. A suspension of 3.15 g of the potassium salt of the dinitronaphthylaminesulfonic acid in 30 ml of a 13.2% potash solution was boiled for 2 hours. The solution was diluted somewhat with water, and the monopotassium salt of the dinitronaphtholsulfonic acid precipitated by acidification with hydrochloric acid; yield 3.15 g. Elongated tetrahedral yellow prisms, quite difficultly soluble in hot water (dipotassium salt—red needles).

Found %: H_2O 6.76 (dried at 130°); N 8.02; K 11.03. $C_{10}H_5O_8N_2SK \cdot 1.5\ H_2O$. Calculated %: H_2O 7.13. $C_{10}H_5O_8N_2SK$. Calculated %: N 7.95; K 11.10.

2,4,6-Trinitro-1-naphthol. To a suspension of 1.89 g of the potassium salt of the dinitronaphtholsulfonic acid in 45 ml of water was added 4.5 ml of 56.2% nitric acid, and the mixture was brought up to the boil in 30 minutes. After cooling,the trinitronaphthol was filtered; yield 1.15 g. Broad yellow needles (from aqueous alcohol), difficultly soluble in water and readily soluble in alcohol and acetic acid; m.p. 157° (decompn.). Sodium salt—yellow needles, potassium salt—orange-yellow needles; both salts are difficultly soluble in cold water.

Found %: N 15.28. $C_{10}H_5O_7N_3$. Calculated %: N 15.05.

6-Nitro-1,2-naphthoquinone-4-sulfonic Acid Dioxime (III). Obtained in the same manner as 1,2-naphthoquinone-4-sulfonic acid dioxime [3]. The yield of pure substance from 8.78 g of the potassium salt of the nitronaphthofuroxan bisulfite compound was 5.5 g (54.2%). The potassium salt was obtained as elongated hexagonal pale-yellow prisms, quite difficultly soluble in cold water. With ferrous sulfate the water solution is colored a deep dull-violet color. When boiled with 1% hydrochloric acid a red-brown solution is formed, which after adding sodium acetate and ferrous sulfate assumes a green color, which indicates the presence of an o-nitrosonaphthol derivative. The substance isolated from the acid solution fails to give this reaction, and apparently is the potassium salt of 6-nitro-1,2-naphthofurazan-4-sulfonic acid (colorless prisms; found %: H_2O 7.41; K 11.49 (in the dry substance).

Found %: C 29.66; H 2.88; N 10.22; K 9.44. $C_{10}H_6O_7N_3SK \cdot 3H_2O$. Calculated %: C 29.62; H 2.98; N 10.36; K 9.64.

6-Nitro-1,2-naphthofuroxan-4-sulfonic acid (V). Obtained in the same manner as 1,2-naphthofuroxan-4-sulfonic acid [3] by the oxidation of 4.24 g of the potassium salt of 6-nitro-1,2-naphthoquinone-4-sulfonic acid dioxime (III); yield of potassium salt 3.23 g (81.8%). Elongated colorless prisms, quite difficultly soluble in hot water.

Found %: H_2O 7.18 (dried at 130°); N 12.01; K 11.10. $C_{10}H_4O_7N_3SK \cdot 1.5\ H_2O$. Calculated %: 7.18. $C_{10}H_4O_7N_3SK$. Calculated %: N 12.03; K 11.19.

6-Nitro-1,2-naphthofurazan-4-sulfonic Acid (IV). To a suspension of 4.24 g of the potassium salt of the nitronaphthoquinonesulfonic acid dioxime in 10 ml of water was added a solution of 2.8 g of 80% potassium hydroxide in 5 ml of water. The obtained solution was kept at 15° for 1 hour and then boiled for 15 minutes. After cooling, the potassium salt of the nitronaphthofurazansulfonic acid was filtered; yield 3.5 g (92.5%). Elongated colorless prisms, quite difficultly soluble in cold water.

Found %: H_2O 7.48 (dried at 120°); N 12.57; K 11.54. $C_{10}H_4O_6N_3SK \cdot 1.5\ H_2O$. Calculated %: H_2O 7.50. $C_{10}H_4O_6N_3SK$. Calculated %: N 12.61; K 11.73.

The potassium salt of the nitronaphthofurazansulfonic acid (IV), formed in obtaining the dinitronaphthylaminesulfonic acid (II), had the same properties and external appearance.

Found %: H_2O 7.48; K 10.76; N(in dry substance) 12.70. $C_{10}H_4O_6N_3SK \cdot 1.5\ H_2O$. Calculated %: K 10.85.

4-Chloro-6-nitro-1,2-naphthofurazan. Obtained in the same manner as 4-chloro-1,2-naphthofurazan [7] from the potassium salt of the nitronaphthofurazansulfonic acid; 0.9 g of the potassium salt gave 0.6 g of the chloro derivative. Elongated curved colorless needles (from alcohol), difficultly soluble in alcohol; m.p. 166.7-167°.

Found %: N 16.77; Cl 14.40. $C_{10}H_4O_3N_3Cl$. Calculated %: N 16.83; Cl 14.20.

6-Amino-1,2-naphthofurazan-4-sulfonic Acid and 4-Chloro-1,2-naphthofurazan. To a solution of 1.8 g of the potassium salt of the nitronaphthofurazansulfonic acid in 43 ml of water was added a solution of 11.0 g of 77% stannous chloride in 16 ml of 35% hydrochloric acid; the mixture was boiled for 1 hour, cooled, and the reduction product filtered; yield 1.28 g. The substance was reprecipitated from a sodium sulfite solution. Colorless needles, very difficultly soluble in water. With 2-naphthol-3,6-disulfonic acid the diazo compound gives an orange-red color, and with resorcinol it gives a yellow-brown color.

Found %: H_2O 11.86 (dried at 130°); N 15.05. $C_{10}H_7O_4N_3S \cdot 2H_2O$. Calculated %: H_2O 11.96. $C_{10}H_7O_4N_3S$. Calculated %: N 15.84.

The diazo compounds, obtained from 1.28 g of the sulfonic acid, was boiled with 15 ml of alcohol for 3 hours, and the alcohol was distilled off. The residue was treated with hydrochloric acid and potassium hypochlorite, and the chloronaphthofurazan was steam-distilled and recrystallized from alcohol. Colorless needles with m.p. 93.4-94.7°; a mixture of the substance with 4-chloro-1,2-naphthofurazan (with m.p. 96-96.2°) melted at 94.8-95.7°.

SUMMARY

1. The bisulfite compound of 1,2-naphthofuroxan, the same as the bisulfite compound of 1,2-naphthofurazan, is converted to the 6-nitro derivative when nitrated in sulfuric acid solution.

2. When treated with weak potash solution the bisulfite compound of 6-nitro-1,2-naphthofuroxan is converted to a mixture of 2,6-dinitro-1-naphthylamine-4-sulfonic acid, 6-nitro-1,2-naphthofurazan-4-sulfonic acid and other substances, and when treated with potassium hydroxide it is converted to 6-nitro-1,2-naphthoquinone-4-sulfonic acid dioxime.

3. 2,6-Dinitro-1-naphthylamine-4-sulfonic acid, when heated with 40% sulfuric acid is converted to 2,6-dinitro-1-naphthylamine, and when heated with potash solution – to 2,6-dinitro-1-naphthol-4-sulfonic acid; the latter with dilute nitric acid is converted to 2,4,6-trinitro-1-naphthol.

4. 6-Nitro-1,2-naphthoquinone-4-sulfonic acid dioxime when oxidized with nitric acid is converted to 6-nitro-1,2-naphthofuroxan-4-sulfonic acid, and when treated with potassium hydroxide – to 6-nitro-1,2-naphthofurazan-4-sulfonic acid; the latter with potassium hypochlorite and hydrochloric acid is converted to 4-chloro-6-nitro-1,2-naphthofurazan.

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K. E. Voroshilov Scientific-Research Institute
of Organic Intermediates and Dyes

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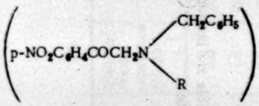
*T.p. = C. B. Translation pagination.

FATTY AROMATIC AMINO ALCOHOLS

II. α-(p-AMINOPHENYL)-β-ALKYLAMINOETHANOLS

S. I. Sergievskaya and L. E. Sventsitskaya

To obtain the α-(p-aminophenyl)-β-alkylaminoethanols ($p\text{-}NH_2C_6H_4CHOHCH_2NHR$) we used p-nitroacetophenone as the starting substance; this ketone was brominated, and the p-nitro-ω-bromoacetophenone obtained in this manner was then reacted with benzylalkylamines containing different alkyl groups (CH_3, C_2H_5, C_3H_7, iso-C_3H_7, C_4H_9, C_5H_{11}); the p-nitrobenzylalkylaminoacetophenones (Table 1) obtained in this manner were then catalytically reduced to the α-(p-aminophenyl)-β-alkylaminoethanols. In running the indicated reactions difficulties were encountered in the isolation and purification of the p-nitrobenzylalkylaminoacetophenones and most of the α-(p-aminophenyl)-β-alkylaminoethanols. The reaction between p-nitro-ω-bromoacetophenone and the benzylalkylamines was accompanied by the formation of tarry substances, for which reason the obtained substances—the hydrochlorides of the p-nitrobenzylalkylaminoacetophenones—had to be subjected to tedious purification (repeated washing with organic solvents, reprecipitation and recrystallization), which strongly lowered their yields.



$$\left(p\text{-}NO_2C_6H_4COCH_2N\begin{matrix}CH_2C_6H_5\\ R\end{matrix}\right)$$

Of the α-(p-aminophenyl)-alkylaminoethanols (Table 2) obtained by us, only the hydrochloride of α-(p-aminophenyl)-β-butylaminoethanol was obtained in crystalline form directly from the solution after hydrogenation and was easily purified by recrystallization, while in the remaining cases, after hydrogenation of the hydrochlorides of the p-nitrobenzylalkylaminoacetophenones and removal of the solvent by distillation, amorphous substances were isolated from the reaction mixture, which could not be purified except by recrystallization. We treated these substances with alcoholic ammonia solution, and the amino alcohols (bases) isolated in this manner were then purified. The hydrochlorides (Table 3) of the purified amino alcohols were obtained in the usual manner.

EXPERIMENTAL

p-Nitro-ω-benzylmethylaminoacetophenone Hydrochloride. In a three-necked flask, fitted with stirrer, thermometer and dropping funnel, was placed 24.4 g of p-nitro-ω-bromoacetophenone* and 150 ml of anhydrous benzene, mixture was cooled to 15°, and then with stirring a solution of 24.2 g of benzylmethylamine in 25 ml of anhydrous benzene was gradually added at such a rate that the temperature of the reaction mixture did not exceed 15-18°. After all of the benzymethylamine had been added the stirring was continued for another 3 hours. The benzene solution of the p-nitro-ω-benzylmethylaminoacetophenone was filtered from the benzylmethylamine hydrobromide precipitate; yield 18.5 g (92.04%). The benzene was vacuum-distilled from the filtrate on the water bath at a bath temperature of 40-45°, while the residual red oil was dissolved in anhydrous ether, ether added until the solution ceased to turn turbid. The ether solution was filtered, and to it from a burette was added in drops an ether solution of hydrogen chloride until it showed acid to Congo. Washing the precipitate with ether and then drying gave 31.1 g of substance, which after washing with acetone melted at 177° (with decompn.). Yield 18.8 g. After recrystallization from alcohol, m.p. 178.5° (with decompn.). The hydrochloride of p-nitro-ω-benzylmethylaminoacetophenone was obtained as slightly tinged crystals,

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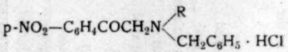
* Obtained in accord with the literature directions [1].

TABLE 1



$p\text{-}NO_2-C_6H_4COCH_2N\langle^{R}_{CH_2C_6H_5} \cdot HCl$

R	Amount starting reagents		Purification method	Melting point	Yield of crude substance in g	Found (in %)			Calculated (in %)		
	p-nitro-ω-bromo-acetophenone	benzylalkylamines $HN\langle^{CH_2C_6H_5}_{R}$				C	H	N	C	H	N
C_2H_5 . . .	30.0 g	33.2 g	Washing with ether and hot ethyl acetate, recrystallization from alcohol.	145.5—146.5°	32.8	60.81	5.91	8.40	61.0	5.72	8.37
iso-C_3H_7	30.5	37.3	Washing with ethyl acetate and ether, recrystallization from ethyl alcohol.	159	33.0	61.82	6.02	7.82	61.98	6.07	8.03
C_3H_7 . . .	12.2	14.9	Washing with ethyl acetate and recrystallization from alcohol.	162.5	14.3	61.84	5.93	8.04	61.98	6.07	8.03
C_4H_9 . . .	24.4	32.6	Washing with acetone, recrystallization first from water, and then from alcohol.	146.5—147 (decomp.)	28.0	62.90	6.56	7.88	62.89	6.39	7.72
C_5H_{11} . . .	24.4	35.46	Recrystallization from ethyl acetate and alcohol.	140.5 (decomp.)	31.6	—	—	7.41	—	—	7.43

Remarks. The p-nitrobenzylalkylaminoacetophenone hydrochlorides given in the table are insoluble in ether and benzene, difficultly soluble in acetone and ethylacetone, and quite readily soluble in water, methyl alcohol and ethyl alcohol.

difficultly soluble in methyl and ethyl alcohol water, chloroform and acetone, and insoluble in ether and benzene.

Found %: C 59.87; H 5.24; N 8.37. $C_{16}H_{16}N_2O_3 \cdot HCl$. Calculated %: C 59.92; H 5.35; N 8.74.

The remaining hydrochlorides of the p-nitrobenzylalkylaminoacetophenones were obtained in the same manner as the hydrochloride of p-nitrobenzylmethylaminoacetophenone; some data on these compounds are to be found in Table 1.

α-(p-Aminophenyl)-β-methylaminoethanol. In a hydrogenation bottle was placed 8 g of p-nitro-ω-benzylmethylaminoacetophenone hydrochloride, 100 ml of ethyl alcohol and a solution of 0.8 g of palladium chloride in 3 ml of water and 1.2 ml of concentrated hydrochloric acid. On shaking in a hydrogen atmosphere at 30-35° for 1 hour the hydrogen absorption was 3.2 liters (21°, 753 mm) (theoretical amount of hydrogen under the given conditions 3.21 liters). On termination of hydrogen absorption the catalyst was separated from the reaction mass, the ethyl alcohol, water and toluene* removed by vacuum-distillation on the water bath, the residual oil freed from moisture traces by a 3-fold treatment with anhydrous ethyl alcohol and subsequent removal of the alcohol after each treatment, and then it was dissolved in anhydrous ethyl alcohol and the solution was saturated with ammonia gas. Ether was added to the reaction mass to completely precipitate the ammonium chloride, after which the ammonium chloride was filtered, the alcohol and ether removed from the filtrate by distillation, and the residual oil (4.65 g) rubbed in a

TABLE 2

$p\text{-}NH_2\text{-}C_6H_4CHOHCH_2NHR$

R	Amount of corresponding nitroaminoketone (in g)	$PdCl_2$ (in g)	Ethyl alcohol (in ml)	Amount of absorbed hydrogen (in liters)	Melting point	Yield of crude substance (in g)	Found (in %)			Calculated (in %)		
							C	H	N	C	H	N
CH_3	8.0	0.8	100	3.2 (21°, 753.5mm)	124—124.5°	3.0	65.31	8.21	16.46	65.03	8.48	16.84
C_2H_5	5.25	0.5	75	2.05 (20°, 750mm)	135.5—134.5	1.85	66.67	8.99	15.64	66.63	8.94	15.54
iso-C_3H_7	8.0	0.8	100	2.9 (20°, 760.5mm)	137—138	3.0	68.39	9.28	14.35	68.00	9.34	14.41
C_3H_7	6.25	0.6	90	2.25 (17°, 745.5mm)	89.5—90	2.3	68.48	9.23	14.18	68.00	9.34	14.41
C_4H_9	7.5	0.7	75	2.55 (16°, 764 mm)	89—90	2.98	69.37	9.56	13.31	69.15	9.68	13.45
C_5H_{11}	7.8	1.25	78	2.75 (20°, 748mm)	72.5—73	1.6	70.42	9.81	12.54	70.23	9.97	12.60

Remarks. The α-(p-aminophenyl)-β-alkylaminoethanols are difficultly soluble in water, ether and acetone, insoluble in benzene, and readily soluble in ethyl and methyl alcohols; they were purified by recrystallization from ethyl alcohol.

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* In other experiments the oil remaining after distilling off the indicated solvents was rubbed with small amounts of anhydrous ethyl alcohol until a crystalline substance separated; this substance was dissolved in alcohol, and dry ether was added to the alcohol solution. The substance that precipitated here melted at 218°. This substance was dissolved in alcohol, and the alcohol solution was saturated with ammonia gas. After distilling off the alcohol the residue was vacuum-distilled. The substance distilled at 0.5 mm in a wide temperature interval (127-153°). When the distilled substance was treated with ether a very small amount of ether-soluble crystalline substance with m.p. 116-119° was isolated; after recrystallization from alcohol, m.p. 124°. The elementary analysis data corresponded to the composition of α-(aminophenyl)-β-methylaminoethanol.

small amount of ether with some seed crystals of α-(p-aminophenyl)-β-methylaminoethanol, obtained by a different technique.* The yield of substance with m.p. 118-120° was 3 g (72.2 %). After recrystallization from ethyl alcohol, m.p. 124-124.5°. α-(p-Aminophenyl)-β-methylaminoethanol was obtained as colorless crystals, soluble in ethyl and methyl alcohols, difficultly soluble in ether, acetone and water, and insoluble in benzene.

Found %: C 65.31; H 8.21; N 16.46. $C_9H_{14}N_2O$. Calculated %: C 65.03; H 8.48; N 16.84.

α-(p-Aminophenyl)-β-methylaminoethanol Dihydrochloride. A solution of 0.2 g of α-(p-aminophenyl)-β-methylaminoethanol in 5 ml of anhydrous ethyl alcohol was treated with an ether solution of hydrogen chloride to give the hydrochloride, which separated as a colorless amorphous precipitate. Decomposition point ~ 130°.

Found %: N 11.91; Cl 29.46. $C_9H_{19}N_2 \cdot 2HCl$. Calculated %: N 11.71; Cl 29.65.

α-(p-Aminophenyl)-β-(n-butyl)-aminoethanol. When a solution of 7.5 g of p-nitro-ω-benzyl-(n-butyl)-aminoacetophenone hydrochloride in 75 ml of ethyl alcohol was shaken in a hydrogen atmosphere in the presence of 0.7 g of palladium chloride, previously dissolved in 3 ml of water and 0.75 ml of concentrated hydrochloric acid, at 30-35° for 1 hour and 15 minutes the hydrogen absorption was 2.55 liters (16°, 764 mm), after which the hydrogen absorption ceased (theoretical amount of hydrogen under the given conditions 2.59 liters). The catalyst was separated from the reaction mass, and the alcohol, water and toluene were removed by vacuum-distillation on the water bath; moisture traces were removed by a 3-fold treatment with anhydrous ethyl alcohol with removal of the alcohol after each treatment. The obtained crystals were washed with anhydrous ethyl alcohol. The yield of colorless crystals with m.p. 135-137° was 4.9 g (84.4 %). The dihydrochloride of α-(p-aminophenyl)-β-(n-butyl)-aminoethanol is readily soluble in water, difficultly soluble in ethyl alcohol, and insoluble in ether, benzene and acetone.

TABLE 3

$p\text{-}NH_2\text{-}C_6H_4CHOHCH_2NHR \cdot 2HCl$

R	Calculated (in %)			Found (in %)		
	C	H	N	C	H	N
CH_3	45.29	6.74	11.71	45.45	6.65	11.91
C_2H_5	—	—	11.06	—	—	11.15
$CH(CH_3)_2$	49.44	7.54	10.48	49.53	7.56	10.30
$CH_2CH_2CH_2CH_3$	51.25	7.89	9.96	51.66	7.76	10.02
$CH_2CH_2CH_2CH_2CH_3$	52.88	8.19	9.49	52.85	8.18	9.33

Found %: C 51.66; H 7.76; N 10.02. $C_{12}H_{20}N_2O \cdot 2HCl$. Calculated %: C 51.25; H 7.89; N 9.96.

A solution of 2.3 g of α-(p-aminophenyl)-β-(n-butyl)-aminoethanol in 2.3 ml of water was treated with ammonia gas to give a crystalline precipitate on cooling. The precipitate was washed with water and dried. The yield of substance with m.p. 83-85° was 1.4 g (82.4 %). After recrystallization from ethyl alcohol, m.p. 89-90°. α-(p-Aminophenyl)-β-(n-butyl)-aminoethanol was obtained as colorless crystals, soluble in ethyl alcohol, difficultly soluble in water, acetone and ether, and insoluble in benzene.

Found %: C 69.37; H 9.56; N 13.31. $C_{12}H_{20}ON_2$. Calculated %: C 69.19; H 9.68; N 13.45.

The remaining α-(p-aminophenyl)-β-alkylaminoethanols and their dihydrochlorides prepared by us were obtained in exactly the same manner as the α-(p-aminophenyl)-β-methylaminoethanol and its dihydrochloride. The α-(p-aminophenyl)-β-alkylaminoethanols and the corresponding dihydrochlorides that we prepared are briefly described in Tables 2 and 3.

SUMMARY

1. The hydrochlorides of the p-nitrobenzylalkylaminoacetophenones with alkyl groups from CH_3 to C_5H_{11} were prepared.

2. The α-(p-aminophenyl)-alkylaminoethanols with alkyl groups from CH_3 to C_5H_{11}, and also their hydrochlorides, were prepared.

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* See footnote, preceding page.

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S. Ordzhonikidze All-Union
Scientific-Research
Chemical-Pharmaceutical Institute

DISCUSSION

THE NOMENCLATURE OF COMPOUNDS OBTAINED BY TREATING CARBOXYLIC ACID AMIDES WITH PHOSPHORUS PENTACHLORIDE

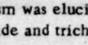
A. V. Kirsanov

For the compounds obtained in treating the amides of carboxylic acids with phosphorus pentachloride and having, as it were, the structures $RCCl_2NH_2$ and $RCCl{=}NH$, Wallach in 1884 [1] proposed the names "amide chloride" and "imide chlorides", which after this became firmly established in the chemical literature. In the meanwhile, in 1931 Hantzsch [2] showed that the reaction of hydrogen halides with nitriles gave not compounds of structures $RCHal_2NH_2$ and $RCHal = NH$, but nitrilium salts of structures $(RC \equiv NH)^+Cl^-$ and $[(RC \equiv NH)^+Cl^-]HCl$. In addition, Hantzsch rigidily proved that the hydrochloride salts, obtained from nitriles and hydrogen chloride, are identical with the substances formed in the treatment of carboxylic acid amides with phosphorus pentachloride. As a result, there is no doubt but that the "amide chlorides" of Gautier, Gerhardt and Wallach are actually nitrilium salts, while the "imide chlorides" of the $RCCl{=}NH$ type have not been obtained up to now and, in general, are probably incapable of existence.

Recently [3] a mechanism was elucidated for the reaction of phosphorus pentachloride with carboxylic acid amides. Hydrogen chloride and trichlorophosphazoacyls are obtained in this reaction, while the nitrilium salts appear as the products of secondary reactions—the thermal cleavage of the trichlorophosphazoacyls into phosphorus oxychloride and nitriles, and subsequent reaction of the nitriles with hydrogen chloride. As a result, neither "amide chlorides" nor "imide chlorides" are formed in the reaction of phosphorus pentachloride with carboxylic acid amides. Nevertheless, old inaccurate data is still being presented in contemporary textbooks [4] and the use of these terms is retained.

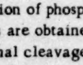
It might be postulated that the "amide chlorides" could be obtained from nitrogen-substituted acid amides. However, such a postulation was not verified. At the present time there fail to be any reliable data on the preparation of compounds of the type $RCCl_2N(R'R'')$. When phosphorus pentachloride is reacted with nitrogen-disubstituted carboxylic acid amides the reaction either fails to go, or proceeds with the cleavage of R'Cl and the formation of compounds of the type $RCCl{=}NR'$ [5]. As a result the "amide chlorides", both substituted and unsubstituted, apparently do not exist (or have not been obtained up to now), and consequently the given term is in general unnecessary.

Compounds of the type $RCCl{=}NR'$ are easily obtained, have been comparatively well studied, and are regarded as being "imide chloride" derivatives. The use of the term "imide chloride" should be acknowledged to be exceedingly unfortunate, since it fails to reflect the nature of compounds of this type, in both essence and form being the chlorides of imino acids:



$RC({=}NR')OH$

Imino Acid



$RC({=}NR')Cl$

Imino acid chloride

Compounds of type $RC({=}NR')Cl$ should be named imino acid chlorides or iminoacyl chlorides. For example,

$C_6H_5C(=NCH_3)Cl$ is the chloride of N-methyliminobenzoic acid or N-methyliminobenzoyl chloride; and $CCl_3C(=NPOCl_2)Cl$ is the chloride of the N-phosphoric acid of trichloroiminoacetyl chloride. The term "imide chloride", as proposed due to misunderstanding, is unnecessary, and should be excluded from chemical nomenclature.

SUMMARY

It was proposed to exclude the terms "amide chloride" and "imide chloride" from chemical nomenclature.

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* T.p. = C. B. Translation pagination.

ON THE PROBLEM OF STEPWISE COMPLEX FORMATION*

K. B. Yatsimirsky

In a published paper [1] L. P. Adamovich and M. S. Novakovsky come out with a criticism of the method proposed by us for calculating the constants of unstable complexes in stepwise complex formation. Their objection reduces to the statement that "it is known from experiment that in the process of stepwise dissociation there can simultaneously cleave not 1, but several, for example, 2 ions". In such case the method proposed by us for calculating the instability constants is inapplicable. In connection with the above it is first of all necessary to mention that the remarks of the authors refer not only to the method proposed by us, but also to all of the other currently existing methods for calculating the instability constants in stepwise complex formation. Such methods are, for example, the methods of Bjerrum [2], Leden [3] Fronaeus [4] and others. Recently these methods have been subjected to thorough analysis and have been expanded further [5-7].

The possibility of forming all of the intermediate forms in the dissociation of a complex follows directly from the theory of stepwise complex formation, proposed by Bjerrum [2] and receiving expansion and support in the numerous studies of A. K. Babko. For some reason the authors of the mentioned paper were completely silent on this important point. Consequently, the discussion deals not only with the method proposed by us, but with all of the methods that currently exist for calculating the instability constants in stepwise complex formation, and even with the theory of stepwise complex formation itself. Finally, the authors indicate that contradictions exist in our published paper [8].

The statement made by us of the possible absence of certain intermediate forms in stepwise complex formation was highly conjectural and in part was based on our proposed attempt to interpret the data on the thermochemistry of the nickel ammine complexes [9]. Incidentally, we will mention here that a more thorough analysis of the experimental data convinced us that it is possible to interpret them by another method, without disturbing one of the basic tenets of the theory of stepwise complex formation.

To refute the basic tenets of the theory of stepwise complex formation some experimental facts should be presented (if the authors have such at their disposal), and not limit the discussion to the phrase that we cited above. However, the questions raised by the authors serve as evidence that actually some new methods should be found to verify experimentally the formation of all of the intermediate complex forms in stepwise complex formation.

It is possible that the formation and existence of intermediate complex forms can be verified by the method studying the absorption spectra in the infrared region and the Raman spectra. This method was recently used by Jones and Penneman to study the cyanide complexes of silver [10]. In this case the authors were able to conclusively show the existence of intermediate forms.

L. P. Adamovich and M. S. Novakovsky also state that "analysis of the $E_{\frac{1}{2}}$ - log C relationship can lead to a demonstration of the existence of complex compounds with a definite coordination number only when considerable linear portions (corresponding, for example, to a change of 2 units in log C) are observed on the curve". Such should be encountered only in the absence of stepwise complex formation or with an enormous difference in the stepwise instability constants of the individual complexes (by several orders) [11]. In the vast majority of actual cases the stepwise instability constants differ by one to two orders, and in the systems there coexist two, three, or a greater number of complexes with different coordination numbers.

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* In connection with the paper by L. P. Adamovich and M. S. Novakovsky "Problem of Determination of the Composition of Complexes by Stepwise Complex Formation," published in J. Gen. Chem. 25, 1308 (1955) (C. B. Translation p. 1253).

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FURTHER DISCUSSION ON THE POLAROGRAPHIC DETERMINATION OF THE COMPOSITION AND STABILITY OF COMPLEX IONS IN SOLUTION IN STEPWISE COMPLEX FORMATION

Ya. I. Turyan

As is known, in stepwise complex formation the graphical relationship between the half-wave potential $(E_{\frac{1}{2}})_c$ and the logarithm of the addend concentration ($\log C_X$) is expressed by a curve (in contrast to the corresponding straight line when only one complex ion is present [1]), and this complicates a quantitative treatment of the results.

K. B. Yatsimirsky [2,3] proposed a comparatively simple method of finding the consecutive instability constants with the aid of the curve $(E_{\frac{1}{2}})_c - \log C_X$, under the conditions that in solution complex ions exist with coordination numbers (p): 1,2,3,4, etc.

L. P. Adamovich and M. S. Novakovsky [4] raised the point that the complexes with certain coordination numbers in the 1,2,3,4, etc. series cannot be formed due to steric hindrance or some other difficulties. On this basis the authors [4] conclude that the K. B. Yatsimirsky method makes it impossible to accurately establish the composition of the intermediate complex ions, and only indicates the minimum and maximum coordination numbers, corresponding to a given addend concentration interval. Being in complete agreement with the argument of L. P. Adamovich and M. S. Novakovsky, we believe, for the case where the condition p = 1,2,3,4, etc. is disturbed, that also the minimum and maximum coordination numbers cannot be determined by the K. B. Yatsimirsky method, since for a different addend concentration interval these coordination numbers become intermediate.

The remarks made by L. P. Adamovich and M. S. Novakovsky undoubtedly deserve consideration. Nevertheless, the voluminous experimental material on stepwise complex formation in solutions shows that the condition p = 1,2,3,4, etc. is observed most frequently.

At the same time there are other difficulties associated with the use of the K. B. Yatsimirsky method. This caused us to reexamine the problem of the polarographic study of stepwise complex formation.

In addition to the indicated condition, in deriving the relationship between $(E_{\frac{1}{2}})_c$ and C_X, K. B. Yatsimirsky [2,3] makes use of still another condition: the domination of only two forms of the complex ions MX_p and MX_{p+1} (we neglect the charges on the ions) when the concentrations $C_{MX_p} = C_{MX_{p+1}}$ are equal. This condition, when compared with the first, should apparently be much less frequently observed experimentally. As a matter of fact, there may even be cases where some pairs of complexes MX_p and MX_{p+1} fail to dominate at all addend concentrations. On the other hand, it may be observed that there is domination of MX_p and MX_{p+1}, but not at $C_{MX_p} = C_{MX_{p+1}}$. Strictly speaking, the K. B. Yatsimirsky method is inapplicable in both examples. It is evident that fulfillment or nonfulfillment of the examined condition depends on the ratio values of the instability constants of different complex ions, and since the instability constants are the values being sought, then the validity of the condition that the forms MX_p and MX_{p+1}, dominate cannot be verified on the basis of the constants found in this manner.

As a result, in using the K. B. Yatsimirsky method it is necessary to keep a number of limitations in mind. This is understandable if it is considered that the K. B. Yatsimirsky equation is an approximate solution of the general relationship between $(E_{\frac{1}{2}})_c$ and C_X that was obtained by DeFord and Hume [5]. In connection with this, for a more complete examination of the problem it is expedient to also turn to the exact solution of this equation, given in the same study [5].

For this we will first assume that in solution at addend concentration C_X there exist complex ions with random coordination numbers in the interval 1 − J: 1,2,3...p, p + 1, ... J and corresponding instability constants K_1, K_2, K_3 ... K_p, K_{p+1}... K_J. In addition, the simple ions of the metal are also present in the solution. If it is assumed as a first approximation that the diffusion current constants of the indicated ions are the same, and, for simplicity, assume that the activity coefficients are equal to unity, then it is possible to derive, in accord with the work of DeFord and Hume [5], the following general relationship between $(E_{\frac{1}{2}})_c$ and C_X:

$$(E_{1/2})_c = (E_{1/2})_s - \frac{RT}{nF}\ln\left(1+\frac{C_x}{K_1}+\frac{C_x^2}{K_2}+\cdots+\frac{C_x^p}{K_p}+\frac{C_x^{p+1}}{K_{p+1}}+\cdots+\frac{C_x^J}{K_J}\right), \quad (1)$$

where $(E_{\frac{1}{2}})_s$ is the half-wave potential of the simple metal ion. From this equation it is easy to obtain the K. B. Yatsimirsky equation, if it is assumed that in solution only two forms of the complex ions MX_p and MX_{p+1} dominate. Actually, in this case all of the terms in parentheses, can be neglected with the exception of C_X^p/K_p and C_X^{p+1}/K_{p+1}, which leads to the K. B. Yatsimirsky equation:

$$(E_{1/2})_c = (E_{1/2})_s - \frac{RT}{nF}\ln\left(\frac{C_x^p}{K_p}+\frac{C_x^{p+1}}{K_{p+1}}\right). \quad (2)$$

The given equation, under the conditions p = 1,2,3,4, etc. and domination MX_p and MX_{p+1} at $C_{MX_{p+1}}$, K. B. Yatsimirsky solves by the method of tangents to the curve $(E_{\frac{1}{2}})_c - \log C_X$.

The essence of an exact solution of equation (1), where fulfillment of the indicated conditions is not required, reduces to a use of the graphical method of Leden [6], already examined in our literature [3]. It is necessary to mention that DeFord and Hume [5] fail to consider that although at first in the derivation of equation (1) random coordination numbers are assigned in the interval 1-J, nevertheless the use of the Leden method permits them to solve the problem of actually existing coordination numbers. As a matter of fact, if the Leden function [6] F(X) at $C_x = 0$ is obtained, differing from zero by a value greater than experimental error, then this means that the corresponding complex ion actually exists. F(X) can have only a positive value or zero. If at $C_x = 0$, F(X) is equal to zero or differs from zero by a value less than experimental error, then it is impossible to solve the problem of whether in general the given complex ion is formed, or whether being formed, it possesses very small stability. From the practical viewpoint both of these conclusions are identical.

In conclusion we will compare the instability constants, obtained with the aid of the exact method of DeFord and Hume, with the corresponding constants obtained on the basis of the approximate, but simpler method of K. B. Yatsimirsky. For this we made use of the data from the studies of Hume, DeFord and Cave [7], Frank and Hume [8], and Nyman [9], and determined the instability constants with the aid of the K. B. Yatsimirsky method. The indicated authors used the DeFord and Hume method. A comparison of the formation constants, K' = 1/K, found with the aid of the

Complex	Method	K'_1	K'_2	K'_3	K'_4
Thiocyanate complexes of cadmium [7]	DeFord and Hume	11	56	6*	60
	Yatsimirsky	18	62	87	49
Thiocyanate complexes of zinc [8]	DeFord and Hume	3	7	1	20
	Yatsimirsky	5	10	14	9
Pyridine complexes of zinc [9] **	DeFord and Hume	26	13	–	–
	Yatsimirsky	18	68	–	–

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* As indicated in study [7], this value had been obtained more accurately earlier by Leden [6].

** We do not present the constants K'_3 and K'_4, since only the order of their values was obtained in study [9].

two methods, is given in the Table. From this Table it can be seen that a number of the constants, obtained by the two methods, show quite good agreement. However, there are also considerable differences (for example, K'_3 for Cd + CNS and Zn + CNS, and K'_2 for Zn + Py), conditioned by the approximate nature of the K. B. Yatsimirsky method. In particular, this approximate nature is explained by the fact that in the systems Cd + CNS and Zn + CNS the complex ion MX_3, either in pair with MX_2 or in pair with MX_4, fails to dominate at all values of C_x. In addition, the condition of the complexes MX_p and MX_{p+1} showing domination at the point of equal concentrations $C_{MX_p} = C_{MX_{p+1}}$ is also not always fulfilled in the examined systems. Thus, at $C_{ZnCNS} = C_{Zn(CNS)_2}$ the C_{Zn} concentration still constitutes ≈ 30 %. This also could have introduced some error in finding the constants with the aid of the K. B. Yatsimirsky method.

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Kishinev State University

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FROM THE COMMISSION ON NOMENCLATURE OF CHEMICAL COMPOUNDS OF THE CHEMICAL SCIENCES DIVISION OF THE ACADEMY OF SCIENCES OF THE USSR

The Chemical Sciences Division of the Academy of Sciences of the USSR set up a Commission on the Nomenclature of Chemical Compounds, whose function is to collect and study the information gleaned from

Name	Symbol	Atomic no.	Atomic weight
Nitrogen	N	7	14.008
Actinium	Ac	89	287
Aluminum	Al	13	26.98
Americium	Am	95	[243]
Argon	A	18	39.944
Astatine	At	85	[210]
Barium	Ba	56	137.36
Beryllium	Be	4	9.013
Berkelium	Bk	97	[249]
Boron	B	5	10.82
Bromine	Br	35	79.916
Vanadium	V	23	50.95
Bismuth	Bi	83	209.00
Hydrogen	H	1	1.0080
Tungsten	W	74	183.92
Galodinium	Gd	64	156.9
Gallium	Ga	31	69.72
Hafnium	Hf	72	178.6
Helium	He	2	4.003
Germanium	Ge	32	72.60
Holmium	Ho	67	164.94
Dysprosium	Dy	66	162.46
Europium	Eu	63	152.0
Iron	Fe	26	55.85
Gold	Au	79	197.0
Indium	In	49	114.76
Iodine	I	53	126.91
Iridium	Ir	77	192.2
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.92
Cadmium	Cd	48	112.41
Potassium	K	19	39.100
Californium	Cf	98	[249]
Calcium	Ca	20	40.08
Oxygen	O	8	16
Cobalt	Co	27	58.94
Silicon	Si	14	28.09
Krypton	Kr	36	83.80
Xenon	Xe	54	131.3
Curium	Cm	96	[245]
Lanthanum	La	57	138.92
Lithium	Li	3	6.940
Lutetium	Lu	71	174.99
Magnesium	Mg	12	24.32
Manganese	Mn	25	54.94
Copper	Cu	29	63.54
Mendelevium	Md	101	[256]
Molybdenum	Mo	42	95.95
Arsenic	As	33	74.91
Sodium	Na	11	22.991
Neodynium	Nd	60	144.27
Neon	Ne	10	20.183
Neptunium	Np	93	[237]
Nickel	Ni	28	58.69
Niobium	Nb	41	92.91
Tin	Sn	50	118.70
Osmium	Os	76	190.2
Palladium	Pd	46	106.7
Platinum	Pt	78	195.23
Plutonium	Pu	94	[242]
Polonium	Po	84	210
Praseodynium	Pr	59	140.92
Promethium	Pm	61	[145]
Protactinium	Pa	91	231
Radium	Ra	88	226.05
Radon	Rn	86	222
Rhenium	Re	75	186.31
Rhodium	Rh	45	102.91
Mercury	Hg	80	200.61
Rubidium	Rb	37	85.48
Ruthenium	Ru	44	101.1
Samarium	Sm	62	150.43
Lead	Pb	82	207.21
Selenium	Se	34	78.96
Sulfur	S	16	32.066
Silver	Ag	47	107.880
Scandium	Sc	21	44.96
Strontium	Sr	38	87.63
Antimony	Sb	51	121.76
Thallium	Tl	81	204.39
Tantalum	Ta	73	180.95
Tellurium	Te	52	127.61
Terbium	Tb	65	158.93
Technetium	Tc	43	[99]
Titanium	Ti	22	47.90
Thorium	Th	90	232.05
Thulium	Tu	69	168.94
Carbon	C	6	12.011
Uranium	U	92	238.07
Fermium	Fm	100	[255]
Phosphorus	P	15	30.975
Francium	Fr	87	[223]
Fluorine	F	9	19.00
Chlorine	Cl	17	35.457
Chromium	Cr	24	52.01
Cesium	Cs	55	132.91
Cerium	Ce	58	140.13
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22
Einsteinium	En	99	253
Erbium	Er	68	167.2

different languages on the nomenclature of organic and inorganic compounds, with the object of cultivating and introducing into practice (among the different dialects of the USSR people) the scientific nomenclature of chemical compounds.

At the present time the Commission is working on the nomenclature reports which should appear in print and be discussed at the broad conference to be held by the Division of Chemical Sciences in the first quarter of 1957. This should be preceded by a wide general discussion of the indicated reports.

The following are included in the number of basic documents available to the Commission.

A. Nomenclatuture of Organic Compounds. 1) The Geneva rules of 1892 and their modification in the 4th Edition of Beilstein; 2) the rules of the International Union of Pure and Applied Chemistry, adopted in 1930-1953; 3) the Report of the International Union of Pure and Applied Chemistry for the Systematic Nomenclature of Hydrocarbons and Basic Heterocyclic Rings (1955); 4) the new proposals of Lawson, Taylor and Patterson on the Nomenclature of Condensed Cyclic Structures (1955).

B. Nomenclature of Inorganic Compounds. 1) The information of the Nomenclature Commissions of the Mendeleev Societies, compiled by A. Kh. Bork; 2) the rules of the International Union of Pure and Applied Chemistry.

The information of "A" (1-3) was published in the book by A. P. Terentyev and others "Nomenclature of Organic Compounds". Acad. Sci. USSR Press, Moscow (1955). For the information of "B" (1) see Prog. Chem., 6, 605-821 (a detailed bibliography is included), 924, 1251, 1723 (1937). The other information will be published by the Commission.

The Commission is asking chemical firms, scientific research institutes, higher educational institutions, book publishers, journal editors and individuals to communicate their proposals, remarks or desires on the questions of the nomenclature of organic and inorganic compounds

The correspondence should be addressed to: Commission on Nomenclature, Div. of Chem. Sci., 14 Kaluzhskaya B., Moscow, or directly to the chairman of the Commission, Acad. Sci. USSR Corresponding Member A. P. Terentyev (Chemical Faculty, Moscow State University, B-234, Moscow).

The Commission on the Nomenclature of Chemical Compounds of the Div. Chem. Sci., Acad. Sci. USSR recommends that in both Russian print and pedagogical practice the official names and symbols of the chemical elements, given in the attached table, be used.

In the table are also given the atomic weights of the elements, approved by the International Commission on Atomic Weights in 1953 and made effective in 1956. [International Union of Pure and Applied Chemistry. Proceedings of the 17th Conference (1953); J. Am. Chem. Soc., 76, 2033 (1954)].

For some of the radioactive elements the mass numbers of the most long-lived isotopes, shown in brackets, are presented instead of the atomic weights.

These values are based on literature information as of January 1, 1956. When compared with the values approved by the International Commission, the following changes have been made.

Berkelium. Previous value 245, half-life 4.95 days. Recommended value 249, half-life 290 days. Based on the data of Diamond, Magnusson, et al., [Phys. Revs., 94, 1083 (1954); 96, 1576 (1954)].

Californium. Previous value 248, half-life 250 days. Recommended value 249, half-life 470 ± 100 years. Based on the data of Diamond, Magnusson, et al., [Phys. Revs., 94, 1083 (1954); 96, 1576 (1954)].

Also given in the table are the elements Nos. 99, 100 and 101, obtained by Seaborg and coworkers in 1951-1955, for which the indicated investigators proposed the names: No. 99– Fermium (Fm), No. 100– Einsteinium (E), and No. 101– Mendelevium (Mv) [Phys. Revs., 98, 1518 (1955); Prog. Chem., 25, 135 (1956)].

Accepting these names, the Commission recommends using the symbol En for einsteinium, and the symbol Md for mendelevium, which is in accord with the traditional practice of forming the symbols of elements.

For the isotopes, found in the natural radioactive series, as well as for the isotopes of other elements, it is recommended not to use the now obsolete historical names, but instead the element symbols given in the

official list, indicating the isotope mass number by index. For the isotopes of hydrogen and radon (no. 86) it has been decided, together with the recommended designation method, to use when necessary the following names and symbols: deuterium (D), tritium (T), actinon (An), and thoron (Tn).

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